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Research Needs in Heterogeneous Tropospheric Chemistry

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FOREWORD

The heterogeneous nature of the atmosphere is a central phenomenon in atmospheric science. The role of particles in the atmosphere has been a major concern in studies of weather, climate, and atmospheric chemistry for many years. The chemical composition and optical properties of atmospheric aerosols, the pathways along which gases emitted into the atmosphere from natural and manmade sources are turned into particles, and the role of particle surfaces in catalyzing reactions are central issues in atmospheric chemistry and in the effects of chemistry on climate.

In a report published in 1981 (Seinfeld et al., 1981), the NASA Working Group on Tropospheric Program Planning, chaired by Dr. John Seinfeld of the California Institute of Technology, recommended a program of research on global-scale atmospheric chemistry as a major opportunity for NASA to make a significant new contribution to atmospheric science. NASA is well suited to make this contribution, given its interests and capabilities and its abilities to make space observations that eventually play a uniquely valuable role.

Heterogeneous atmospheric chemistry was identified in this 1981 report as a critical component of a global atmospheric chemistry program. In January 1984, a group of experts in heterogeneous atmospheric chemistry and closely related subjects, who were also familiar with NASA's current research programs and its capabilities, met in Sarasota, Florida, to make some specific suggestions for research projects to be undertaken within the atmospheric chemistry program at NASA, which would begin the task of implementing the broad objectives identified in the report by Seinfeld et al. (1981).

The task of recommending a few selected projects for immediate implementation to launch an eventually fully responsive heterogeneous component of a global tropospheric research program is not an easy one. There are many attractive paths from which to choose. In some cases, the key questions require technology that doesn't yet exist for their answers, and so a balance must be struck between vigorous application of the tools at hand and development of the new tools that are eventually required. A careful distribution of effort between field measurements and the underlying laboratory and modeling work that supports them must be made.

The group assembled at Sarasota met this challenge squarely. This report is the result of their efforts. They have identified a finite, tractable number of potential research projects that take advantage of the leverage of ongoing activities, that concentrate initially on extremely crucial questions, and that lead smoothly to a fully developed program to address the heterogeneous component of a program in tropospheric chemistry appropriate both to the global-scale problem and to the capabilities and role of NASA in such an effort. Dr. Volker Mohnen of the State University of New York at Albany ably organized and led the group. The group's efforts on behalf of NASA's programs are sincerely appreciated. We at NASA hope that this document will be a useful guide to the atmospheric chemistry community regarding potential research topics in heterogeneous atmospheric chemistry.

Robert J. McNeal, Manager
Tropospheric Chemistry Program
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PREFACE

The tasks of this workshop were accomplished by some 30 nationally and internationally recognized experts in heterogeneous processes relevant to the troposphere. In organizing the workshop and selecting the participants, the chairman was ably assisted by the executive secretary and the other members of the Executive Committee.

When the workshop convened, the participants were organized into four working groups of five to seven scientists each, plus four observers. For the first 3 days, the groups met jointly in plenary sessions to discuss: (1) the workshop objectives, (2) pertinent scientific background material, and (3) progress reports, and then individually to formulate and evaluate research recommendations in designated areas. During the following 2 days, the Writing and Assessment Team drafted recommendations (with rationales) for the report, as well as the Executive Summary. The material drafted by this team was assembled into final form by a group of three on-site and off-site editors.

The success of this workshop resulted from the efforts of many individuals. Each of the participants performed in a dedicated and effective manner, which enabled the timely and successful completion of the project. Special thanks are given to the Executive Committee, the Writing and Assessment Team, and the editors. We are particularly grateful to Dr. Robert J. McNeal, Manager of NASA's Tropospheric Chemistry Program, and Mr. John P. Mugler, Jr., Head, Special Projects Office, Atmospheric Sciences Division, NASA Langley Research Center, for their continuous interest in and support of our work in its entirety, from the planning through final reporting stage. We can truly say without reservation that this document represents a joint effort reflecting a significant contribution from each participant.

Volker A. Mohnen
Conference Chairman

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EXECUTIVE SUMMARY

The National Aeronautics and Space Administration, through its Tropospheric Chemistry Program, has sought the advice of the scientific community in the formation of its research goals in atmospheric chemistry. The NASA Working Group on Tropospheric Program Planning established a foundation to guide program development (Seinfeld et al., 1981). One of the areas identified for expanded research efforts to improve our understanding of key biogeochemical cycles was heterogeneous chemistry. Accordingly, in the summer of 1981, the Conference on Multiphase Processes - Including Heterogeneous Catalysis - Relevant to Atmospheric Chemistry was held in Albany, New York, under the joint sponsorship of NASA and the National Science Foundation. The conference brought together (for an exchange of ideas, information, and methodologies) a number of scientists who were actively studying heterogeneous processes in the atmosphere as well as other researchers studying similar processes in the context of other fields. Papers presented at the Albany conference revealed the broad scope of ongoing research in various aspects of heterogeneous processes as well as the potential importance of such processes to atmospheric science, and resulted in publication of the monograph Heterogeneous Atmospheric Chemistry (Schryer, 1982).

The present workshop was conducted to focus more clearly on a long-range research strategy that will begin to incorporate heterogeneous chemistry components complementary to NASA's existing homogeneous tropospheric chemistry program.

The objectives of this workshop were

1. To provide NASA with a hierarchy of interrelated research problems in tropospheric chemistry in scientifically tractable terms, which can be attacked immediately or at some future time, taking into account NASA's mission, capabilities, facilities, and resources, as well as its current research activities and commitments in tropospheric chemistry

2. To identify a research focus for NASA's potential efforts in the area of heterogeneous tropospheric chemistry

Workshop attendees included approximately 30 invited participants from government, universities, and industry. Each participant was selected on the basis of a demonstrated research expertise in tropospheric chemistry.

As input into the workshop, the workshop chairman distributed the report of the NASA Working Group on Tropospheric Program Planning (Seinfeld et al., 1981), together with material prepared in advance by the workshop participants highlighting ongoing activities as well as suggested long-range plans.

The workshop considerations were organized around the following interrelated research categories:

1. Field Programs, including flights of opportunity

2. Laboratory Measurements, including supporting tasks for development of technology and instrumental components of field programs, as well as kinetic and thermodynamic constants relevant to heterogeneous processes

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3. Modeling, including methods for the use and interpretation of field data, and its insertion into large-scale tropospheric models

4. Technology Development

Initial considerations of the workshop were to decide just what information and experiments in heterogeneous tropospheric chemistry would be the most valuable and rewarding, with respect to the understanding of key tropospheric cycles that are important to life. From this hierarchy of perceived research needs, there emerged a recognition of fundamental limitations in measurement techniques and instrumentation, as well as a recognition of the lack of values of fundamental physical parameters appropriate to the processes involved. Selection of appropriate research tasks to help meet these scientific needs was made on the basis of (1) the complementation of ongoing or planned activities in NASA's current tropospheric chemistry program and (2) the expectation that the tasks are achievable with current or near-future state-of-the-art instrument technology. It was found that most field experiments are presently technologically limited. This is not a situation peculiar to heterogeneous chemistry, but typical of the atmospheric sciences at large, where our curiosity is always outrunning our ability to obtain the kinds and amounts of data desired. By focusing on these technology limitations, however, we hope that the limits of measurement capability can be progressively expanded.

Those experiments and other actions that are of great importance to tropospheric chemistry and can be begun immediately are limited in scope. They include the items listed below.

1. The fast photochemical cycle (fig. 1) requires knowledge of H_2O_2 in the gas phase. Instrumentation to measure this substance must be developed and tested. The global concentration field of H_2O_2 is believed to be a dominant factor in aqueous-phase oxidation reactions in the atmosphere, and thus must be measured as soon as technology is available. Availability of a reliable gas-phase H_2O_2 sensor is also important to the implementation schedule for field studies related to most aqueous-oxidation processes, particularly that of sulfur.

2. Secondary photochemistry inside clouds (fig. 2) involves the radicals HO and HO_2, as well as the H_2O_2 molecule. These species are produced in interstitial cloud air and may enter the aqueous phase and initiate a host of aqueous-phase processes, including production of additional H_2O_2, inside the cloud droplets. An initial evaluation of the efficiency of this process can be made by accurately determining, in the laboratory, the mass accommodation coefficients of HO and HO_2 on liquid water. If these coefficients are found to be markedly less than 10^{-3}, then all experiments relating to secondary photochemistry inside clouds will be of minimal interest to NASA's tropospheric chemistry program. Knowledge of mass accommodation coefficients for other species such as SO_2, NO_3, and N_2O_5 is also desirable but not critical to the initiation of field experiments.

3. Field and laboratory investigations of the N_xO_y cycle are worthwhile and rewarding research activities dependent upon the availability of fast, ultra-high sensitivity NO instrumentation. Such investigations require, however, development of compatible NO_2 and HNO_3 measurement systems, so that the NO_2-NO_3-N_2O_5 (see fig. 3) reaction path can be quantitatively studied with particular emphasis on the proposed heterogeneous formation of aqueous-phase HNO_3 under nighttime conditions. In addition, the measurement of HNO_3 for

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all flights of opportunity would build up a data base essential for better understanding of the nitrogen budget. A significant challenge still exists to design NO_3 and N_2O_5 sensors for field operation and deployment in aircraft.

4. Flights of opportunity would provide certain data requirements and technological improvements which would benefit most tropospheric chemistry field experiments, or be prerequisites to those proposed in this report. Of particular interest are the testing and improvement of sensor instruments which can be useful in following tracer materials through atmospheric processes. Such instruments would include fast-response detectors for elemental carbon at concentrations below 1 ng/m^3, and filter collection techniques for enrichment of aerosol samples for later elemental analyses. Additionally, aerosol-size spectrometers covering the nucleation and accumulation modes with sufficient precision (10^3 m^{-3} per 0.01 μm size interval) are necessary to observe the phase transition and growth processes in the free atmosphere. During flights of opportunity, such new instruments should be deployed to test performance. This realistic test will also provide information about the formation and subsequent growth of new particles in the atmosphere. It will thus signal the ability to initiate field programs investigating gas-to-particle conversion and related processes in clean air.

5. Development of airborne cloud and interstitial air collection systems is important. Any field experiments investigating cloud systems require the sampling of representative, noncontaminated cloud water, and of the interstitial air. Such systems are available but require calibration of collection efficiency with respect to cloud droplet size. These efforts should be undertaken on every flight of opportunity.

6. The accumulation and dissemination of scientific reference material important to heterogeneous processes are needed. While there exist collections of reference material on background thermodynamic and kinetic data for homogeneous processes, similar data for heterogeneous and aqueous-phase chemical reactions relevant to tropospheric chemistry remain scattered in the literature. Such data should be regularly collected, critically reviewed, and disseminated to the scientific community working on related research. One of the immediate beneficiaries of such efforts would be the modeling community.

7. The survey and evaluation of instrument technology are other important areas. Since instrumentation appears to be an important factor governing the initiation of field programs, it is important to keep the scientific community aware of available instrumentation capabilities and ongoing advancements in this field.

These recommendations represent important scientific activities complementing existing tropospheric chemistry programs within NASA, and they increase the type and quality of information gained about the processes under investigation. In addition, they address important gaps in either technology or chemical laboratory data that can and should be closed before major field experiments can be planned in detail and carried out.

The field experiments and associated laboratory investigations judged appropriate for NASA have been divided into several categories that reflect the criteria of scientific importance and the availability and suitability of required instrumentation. They address processes, mechanisms, and budgets. They are conceptual rather

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than detailed operational plans because their implementation will probably proceed on a decadal basis and incorporate technology not presently available. This is particularly true for those experiments addressing budget questions. From the hierarchy of complexity of field experiments addressing the N, S, C, and halogen cycles, a few activities emerge that deserve immediate attention because of their complementary nature to planned NASA tropospheric chemistry projects or their possible integration into flight experiments already scheduled for other primary purposes. These include

1. A Marine Boundary Layer Experiment to address problems relating to the N and S budget, and particularly to investigate some heterogeneous pathways

2. A Biomass-Burning Experiment to address gas-to-particle conversions and the formation and dispersion of elemental carbon in the plume

3. The Single-Cloud Experiment to address gas-to-aqueous and aqueous-to-aerosol or aqueous-to-gas heterogeneous pathways for important chemical species of N, S, and the halogens, which would shed light on the redistribution of materials through evaporation-condensation cycles and cloud venting

Details for the scientific objectives and research outlines are presented in the main body of this report. It must be recognized that the incorporation of heterogeneous processes into tropospheric chemistry research plans is a slow and iterative process, and most current studies in nonurban tropospheric regions are in the early stages of development. A carefully staged merger of heterogeneous research activities with development of required technologies can be achieved within a decadal time scale. In pursuit of this goal, significant progress can be achieved in understanding essential elements of the key chemical cycles that are essential to quantitatively assessing global budgets for N, S, C, and halogens, and to measure the impact of anthropogenic sources on them.

INTRODUCTION AND OVERVIEW

General Remarks

Human activities now constitute a major direct and indirect influence on the chemistry of the atmosphere and on the productive capabilities of land, and are increasingly an influence on the ocean. The assessment of our own impact is hampered, however, by a lack of understanding of underlying physical, chemical, and biological factors that regulate the global environmental system. On a decadal time scale, land, sea, and atmosphere operate as a coupled system not only in their physical interactions but also through chemical and biological processes. The atmosphere, and in particular the troposphere, hosts chemical and physical processes that are vital links in the major global biogeochemical cycles essential in the long run to maintaining life on this planet. A global focus for a long-term tropospheric research program is therefore desirable with the following objective: to provide society with the knowledge needed for it to understand the role of the atmosphere in critical global biogeochemical cycles and to assess the susceptibility of the atmosphere to changes caused by human activities. Such knowledge is an essential prerequisite to sound management of the global atmospheric resource in the future.

Science, in general, and NASA, in particular, have now reached the point at which satellite technologies, advanced computers, modern communication systems, and a variety of sophisticated airborne measurement platforms can be made to work together with more traditional investigative tools and platforms to observe and assess global

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tropospheric chemical and physical processes and the changes in them, which are brought about by human activity. This knowledge can then be distilled into the form of comprehensive models for forecasting future trends and events.

The comprehensive study of global environmental trends requires major commitments from governments and scientists and a high degree of international cooperation in research. Such a study is interdisciplinary by its very nature. In overall efforts to direct its programs towards relevant needs, NASA is committed to the long-range goals of the global habitability concept. Within a global-scale interdisciplinary approach to the study of the global-scale environment, NASA's tropospheric chemistry program is a key component. The increasing recognition of the importance of heterogeneous processes in tropospheric chemistry on all scales (Schryer, 1982) makes their study an integral required part of that program.

Heterogeneous Processes

Water in its various physical states plays a dominant role in atmospheric chemistry; water vapor is the source for the all-important hydroxyl radical that is central to gas-phase chemistry, as well as for the hydrogen peroxide molecule that is a crucial aqueous-phase oxidizing agent. The condensed phases (cloud and precipitation elements) host and promote chemical transformations of species involved in most tropospheric cycles, including sulfur, nitrogen, carbon, and halogen compounds.

During phase transitions, latent heat is released or attained. This induces vertical motions of all magnitudes, including penetration of the tropopause or severe downdrafts, resulting in a redistribution of substances in the air. Evaporating cloud and precipitation elements leave behind a particulate and gaseous residue that is, in principle, chemically and physically altered from its state prior to the condensation event. Precipitating clouds remove a fraction of the suspended gaseous and particulate material from the atmosphere and deposit it to the ground. However, on the average, several condensation-evaporation cycles take place prior to such a wet deposition event, each cycle further altering the material involved. Thus, many constituents in the air are reprocessed several times through clouds, making it unusual for any but the most short-lived trace gas or aerosol to be unaffected by clouds or to escape capture by cloud and precipitation elements.

A complete understanding of the chemical cycles in the troposphere will eventually require detailed knowledge of gas-to-particle conversions and of the processes by which gaseous and particulate species are chemically transformed and redistributed by clouds and precipitation and finally deposited at the Earth's surface. Representations of these processes must be embodied in comprehensive global tropospheric models.

A viable heterogeneous tropospheric chemistry program should address several basic questions relating to the fate of many key substances in the troposphere.

1. What are the principal heterogeneous processes governing the global biogeochemical cycles (C-N-S-halogens, etc.)?

   - Where are the crucial links between homogeneous gas-phase chemistry and heterogeneous tropospheric chemistry for key chemical cycles?

   - How important are phase transition processes (e.g., gas-to-particle conversion) on a global and regional scale in explaining key chemical cycles?

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2. What are the roles of heterogeneous processes in transport, physical and chemical transformations, and removal mechanisms in governing the global concentration field of key species in the biogeochemical cycles, and in governing the behavior of regional-scale air masses altered by man?

   - How important are precipitating and nonprecipitating clouds on a global, regional, and local scale in controlling chemical transformation within key chemical cycles?

   - To what extent do precipitating and nonprecipitating clouds influence the vertical distribution of trace substances in the air, and how does this impact on the global, regional, and local concentration fields of major tropospheric species?

   - How important are processes involving clear-air aerosols, i.e., "ghost clouds"?

3. Recognizing the fact that weather and climate constitute a large and complex interactive system on Earth, what methodologies are needed to obtain representative results from the study of heterogeneous tropospheric processes?

Heterogeneous Redistributions

Meteorologists and atmospheric chemists find it convenient to subdivide the atmosphere and to name the subdivisions descriptively. Thus it is convenient to distinguish the troposphere from the stratosphere, and further to subdivide the former into the "free" troposphere and the boundary layer. The advantages of these subdivisions for communication are obvious. Disadvantages arise from the tendency to treat them as closed systems and to underestimate or ignore the mass transfers between them.

In general, internal boundaries in the atmosphere are moving, forming, or dissipating with mass transfers occurring on a variety of scales. For tropospheric field experiments, it is extremely important to identify, study, and quantify the transfer processes from the boundary layer to the free troposphere, from the upper troposphere to the lower stratosphere, and the reverse of these transfers. With few exceptions, the upward transfer is associated with a wet adiabatic process resulting from condensing water vapor and the formation of clouds. Depending upon the spatial scales and magnitudes of the low-level convergence and the degree of convective instability in the ascending air, the clouds can range in type from small cumulus to large cumulonimbus capable of transporting trace gases and aerosols from the near surface into the lower stratosphere.

Examples of such redistributions are presented in figures 4 through 7 showing the calculated global concentration field for OH and NO_x with and without incorporation of the enhanced vertical transport due to cloud venting. The dramatic changes observed in these and similar simulations clearly show the need for field demonstration and validation experiments.

Heterogeneous chemical and physical processes in such cloud transport situations are clearly important in linking photochemical and other homogeneous gas-phase reactions to aqueous and aerosol sinks. The original gaseous species are not lost to the atmosphere in such a phase transition; they can be concentrated, react with other

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materials in the condensed phase, be reinjected to the gaseous phase in a different form, and undergo other transformations and transport prior to final ejection from the atmosphere by dry or wet deposition. Some major connections between homogeneous gas-phase chemistry and heterogeneous processes leading to condensed-phase chemistry are illustrated in figures 1 through 3 and figure 8.

Chemical Cycles

Following the recommendation of the NASA Working Group on Tropospheric Chemistry (Seinfeld et al., 1981), NASA has initiated field experiments for testing the fast photochemical theory predicting cyclic reactions for HO_x and NO_x in the presence of O_3, CO, and H_2O vapor as illustrated in figure 1. This core chemical reaction scheme includes heterogeneous pathways which, if considered, complement and expand ongoing work and potential for broader understanding of the processes involved. The heterogeneous components are H_2O_2, $HONO_2$, and HO_2NO_2 losses to aqueous phases where they can induce aqueous-phase chemical reactions, including photochromatography. In addition, HO_2 and HO can be incorporated by cloud elements, initiating or triggering a whole host of aqueous-phase chain reactions as illustrated in figure 2, thus opening up a whole new area of secondary photochemistry inside clouds.

NASA's homogeneous NO_x gas-phase research program would be able to provide more comprehensive and definitive understanding of the nitrogen cycle if heterogeneous processes were included. Such processes are shown diagrammatically in figure 3. Examples illustrated are formation of HNO_3 through NO_3-N_2O_5 chain (nighttime chemistry of NO_x) and of HNO_2 at night, as well as losses to the aqueous phase as described earlier.

A large fraction of the naturally emitted gaseous sulfur in the atmosphere appears to be in the form of COS and its precursors. Because of its stability, this gas passes largely unchanged through the tropopause into the stratosphere where it is oxidized to sulfate. This contributes to the "background" level of stratospheric sulfate aerosol, to which sulfur compounds injected by sporadic large volcanic eruptions are periodically added. Thus COS as such has no important role in heterogeneous tropospheric chemistry. However, the existence of a steady-state concentration of stratospheric sulfate means that sulfate must be continuously removed from the stratosphere, necessarily by transfer to the troposphere and thence to the Earth's surface.

Indeed, we must keep in mind the fact that heterogeneous processes constitute the ultimate termination step for most tropospheric chemical reactions. However, we limit this workshop to consideration of phase transition processes involving suspended aerosols and cloud elements, thus excluding the solid Earth, oceans and lakes, and vegetation. With these limitations in mind, we recognize in figure 8 the HO_x-NO_x system, which is of central importance to tropospheric chemistry and presently part of this NASA research program. This figure also shows the relationship of these components to the fundamental tropospheric chemistry of N, S, C, and halogens leading by heterogeneous steps to noncyclic transformations. Not shown in the figure but clearly important are analogous reverse reactions leading to gaseous and modified particulate products from species in condensed phases. Concentration fields resulting from evaporated clouds have been occasionally observed but not intensively studied up to this time.

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Workshop Organization

The principal task of the workshop was to formulate and select the heterogeneous chemistry research tasks appropriate and important for the NASA Tropospheric Research Program. Consideration was given to the fundamental scientific importance to tropospheric chemistry and to NASA's current activities in this area.

The workshop formulated the tasks in accordance with the following interrelated principal research categories:

1. Field Programs, including aircraft, lower atmospheric research satellites, and other remote or in situ sensing platform measurements, as appropriate

2. Laboratory Measurements, including supporting tasks for development of major technology and instrumental components of field programs, as well as fundamental kinetic and thermodynamic constants for phase transition rates and equilibria

3. Modeling, including the development of heterogeneous components for inclusion in large-scale models of tropospheric chemistry, transport, and climate. Methods for the use and interpretation of measurement data and global concentration fields, for the insertion into tropospheric models, were also considered

4. Technology Development, which is crucial to the scheduling of research tasks

This workshop report builds upon the Report of the NASA Working Group on Tropospheric Program Planning (Seinfeld et al., 1981), reflects a conceptual approach, and in addition presents specific, detailed proposals for a heterogeneous component of the tropospheric chemistry program.

HETEROGENEOUS ATMOSPHERIC CHEMISTRY: BACKGROUND

Aqueous-phase chemistry is of importance in liquid-water clouds, in rain, and, as well, in liquid water associated with aerosol particles present in clear (non-cloud) air. Although the amount of liquid water associated with such aerosols is much lower (approximately 4 orders of magnitude) than that associated with clouds, the importance of such clear-air aqueous-phase chemistry cannot be ruled out in view of the small fraction (approximately one-third) of the Earth's atmosphere occupied by clouds, the long lifetime of aerosol particles compared to cloud droplets, and the possible nonuniform distribution of reagent concentrations. Little is known about the interaction of ice-phase water with trace gases, but this may be important as well and must be addressed, at least in an initial, exploratory mode.

It is useful to consider the uptake and reaction of a gas (or gases) into and within a cloud or rain drop, or a clear-air aerosol particle containing liquid water, as consisting of a sequence of steps or processes involving interaction of the gaseous and liquid phases. Through a description of the several steps, it becomes possible to describe the overall heterogeneous process. It is convenient to describe the overall process as consisting of the following subprocesses:

1. Gas-phase mass transport of the reagent gas (or gases) to the air-water interface

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2. Mass transport across the interface and possible establishment of solubility equilibria locally at the interface

3. Establishment of rapid aqueous-phase equilibria involving the dissolved gas(es), e.g., hydration and acid dissociation equilibria

4. Aqueous-phase mass transport of the dissolved species within the droplet

5. Aqueous-phase chemical reaction(s)

6. Mass transport of reaction product(s) in the aqueous phase

7. Subsequent gas-phase mass transport of the evolved gaseous product

Steps 1 through 7 are presented schematically in figure 9. The evolution of volatile product species into the gas phase is possible following steps 5 or 6.

From the foregoing picture, it is seen that description of rates of aqueous-phase reaction of atmospheric trace gases requires consideration of the following processes:

1. Equilibrium solubility

2. Gas-phase mass transport

3. Interfacial mass transport

4. Aqueous-phase mass transport

5. Aqueous-phase reaction kinetics

These several processes and the temperature dependence of each are individually amenable to laboratory investigation. Results from such studies may then be used to evaluate rates of atmospheric aqueous-phase reactions under conditions of interest.

This workshop identified those chemical systems that seemed most pertinent to aqueous-phase atmospheric reactions, with the objective of setting priorities for study within the framework of overall NASA objectives. One reasonable basis for assigning priority for the need to describe a particular process should be the annual global flux through the several processes. It was also agreed that sufficient information is available at the present time to allow initial scoping to be conducted, which can place at least rough estimates on the magnitudes of the various fluxes. Such estimates would use as input data concentrations of pertinent reagents and climatological estimates of global liquid-water content (of both clouds and of aqueous clear-air aerosol). Such initial scoping studies should be augmented by further work addressing the altitude, latitude, diurnal, and seasonal variability of these quantities. Ultimately, as information becomes available, it will be desirable to merge this information with similar more detailed descriptions of species concentrations in order to conduct global evaluations. The priorities thus derived must, of course, be modified by the availability (or estimated date of availability) of the necessary techniques and instrumentation needed for measurement.

Based upon the foregoing considerations and also Seinfeld et al. (1981), reaction systems of concern or potential concern in the overall framework of the NASA

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Global Habitability Program were examined. Classes of compounds of concern or potential concern that were identified are listed below.

1. The HO_x species composed of the free radicals OH and HO_2, and the molecule H_2O_2. Aqueous-phase chemistry of these compounds may effect not only their gas-phase chemistry but also aqueous-phase chemistry of other major classes of compounds.

2. The NO_x species composed of NO, NO_2, NO_3, N_2O_5, HNO_2, HNO_3, and HNO_4. Wet deposition as HNO_3 is a major sink of NO_x. The NO_x aqueous-phase chemistry may also have feedback on gas-phase HO_x chemistry, both as a NO_x sink and as a source of HO by means of HNO_2 photolysis.

3. Organic carbon. Recent work has reported substantial precipitation deposition of carboxylic acids even in remote areas (Likens et al., 1983). It is thought (Chameides and Davis, 1983) that aqueous-phase oxidation of aldehydes to the corresponding carboxylic acid may be responsible for this.

4. The SO_x species composed of SO_2, aqueous S(IV) [$SO_2(aq)$, HSO_3^-, $SO_3^=$], and aqueous S(VI) [HSO_4^-, $SO_4^=$]. Aqueous-phase oxidation of S(IV) is thought to be a principal oxidation mechanism of SO_2, if not the principal mechanism. Little information is available regarding the possible importance of aqueous-phase reactions of reduced sulfur compounds.

5. The halogens. Halogens, particularly from sea salt, may interact by aqueous-phase reaction with nonvolatile acids (e.g., sulfuric acid) to liberate the more volatile hydroacid (e.g., HCl) on evaporation of the cloud droplet. Additionally, there may be some oxidation-reduction chemistry of halogens, resulting in a liberation of gaseous elemental species.

It is also useful to categorize aqueous-phase chemistry according to reaction type. We identify the following classes of reactions of concern in atmospheric aqueous-phase chemistry:

1. Redox (oxidation-reduction) reactions:

   Examples $S(IV) \rightarrow S(VI)$

   $N(III) \rightarrow N(V)$

   $RCHO \rightarrow RCOOH$

2. Acid-base reactions:

   Example $HNO_3 + NH_3 \rightleftharpoons NH_4NO_3$

3. Hydrolysis reactions:

   Examples $N_2O_5 \overset{H_2O}{\rightleftharpoons} 2H^+ + 2NO_3^-$

   $RCHO \overset{H_2O}{\rightleftharpoons} RCH(OH)_2$

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4. Metathetical (displacement) reactions:

Example $H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl$

In the context of global habitability and in view of the present state of understanding, we place highest priority on reactions in the redox category. The atmosphere is an oxidative medium characterized by the presence of strong oxidants of both molecular (O_3, H_2O_2) and free-radical (OH, HO_2) nature, in addition, of course, to free molecular oxygen. Because of the presumed importance of H_2O_2 as an aqueous-phase oxidant, this species and its formation and destruction kinetics assume high importance. Present understanding suggests that there is strong coupling of the free radicals HO_2 and OH with H_2O_2 by aqueous-phase as well as gas-phase reactions so that understanding of this chemistry also assumes high importance. In addition to the strong oxidants, catalytic substances are also recognized to be important or potentially important to the description of atmospheric aqueous-redox reactions. Included here are transition metal compounds (in solution or as suspended solid) and particulate carbon (as suspended solid).

Atmospheric heterogeneous chemistry by definition involves at least two-phase systems and may involve three-phase systems. In the former category are liquid-phase reactions that occur within the droplet volume and which utilize soluble gases entering from the atmosphere. In the case of catalytic reactions, these liquid-phase reactions would be characterized as homogeneous. Reactions catalyzed by dissolved transition metal ions belong to this category.

Much less understood are reactions involving a three-phase system: gas-liquid-solid. In these systems, the presence of the solid core in the droplet may have a twofold chemical role: as a solid catalyst (i.e., a site for heterogeneous catalytic reactions) and as a source of leachable catalytically active species. Such three-phase systems are present in the atmosphere in a range of situations, from cloud droplets containing small solid particles, through hygroscopic and deliquescent aerosol particles, to solid particles covered with a thin layer of water. The surface of liquid-water droplets and also thin water films may be also covered with an organic film that may act as a surfactant and/or a barrier for gaseous species diffusing in or out of the droplet. This area of research, in addition to the need for fundamental chemistry studies, also requires novel methods for the characterization of gas-liquid and liquid-solid interfaces.

A special subcategory of two- and/or three-phase systems is the dynamic situation encountered during the condensational growth of cloud droplets. The cloud droplets are being continuously formed. The chemistry of such a polydispersed population of droplets may be different from the chemistry of a constant-size droplet exposed to the same mixture of trace reactive gases. These differences may be related to an altered rate of uptake of trace gases and to resulting changes in concentration of the dissolved species (Gill, Graedel, and Weschler, 1983).

An appropriate program for advancing understanding of aqueous-phase atmospheric chemistry should include the following components noted earlier:

1. Field programs

2. Laboratory measurements

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3. Modeling

4. Technology development

The role of laboratory measurements is clear from the foregoing discussion. Field measurements are most appropriately directed to examination of concentrations of reagents, intermediates, and products pertinent to atmospheric aqueous-phase chemistry. In well-chosen circumstances, it may be possible to follow evolution of chemical composition as a function of time. More frequently, it may be possible to ascertain major differences in composition (e.g., between pre-cloud and post-cloud air) that will give indication of the occurrence of aqueous-phase reactions. Data obtained are necessary for both model development and model verification.

Various types of modeling are indispensable to examination of the processes of concern. These modeling efforts should be directed to elucidation of the several processes, and, consequently, it is anticipated that it will be advantageous to develop a variety of relatively simple models directed toward these processes.

Instrument development is necessary in support, first, of field measurements, and second, of laboratory measurements; the same technology is not usually applicable to both types of investigations.

IMPORTANT PHYSICOCHEMICAL CYCLES

First, it is useful to consider the individual chemical species involved in the atmospheric cycles, together with some compounds suspected but not yet proven as members of those cycles.

The HO_x Cycle

It appears that the gas-phase HO_x cycle may be influenced by heterogeneous reactions. As far as the gas phase is concerned, heterogeneous processes mainly result in losses of OH, HO_2, and H_2O_2. These losses will be particularly large for the HO_x generated within a cloud. At the same time, the gas phase acts as a source of these species in the aqueous phase.

The H_2O_2 produced within cloud droplets and possibly liberated during their evaporation must also be considered in order to quantify the two proposed inputs into this heterogeneous cycle.

The HO_2 and especially H_2O_2 are long lived enough that interaction with aerosol surfaces may provide losses for the gas phase. In the case of H_2O_2, dry deposition at the Earth's surface may also be significant. Little is known about their mass accommodation coefficients or deposition velocity and even less about the ensuing reactions and their products. Thus, it is difficult to estimate the importance of these loss paths except to give upper limits. The lifetime of HO_2 with respect to reaction with aerosol particles could be as low as 100 sec in the planetary boundary layer. The lifetime of H_2O_2 with respect to dry deposition from the planetary boundary layer may be as low as 10 hours.

Thus, these loss paths could be significant and need to be investigated. Dry deposition velocities of H_2O_2 could be determined using the gradient method as soon as reliable techniques for measuring the H_2O_2 concentrations in the gas phase become

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available. This should have a high priority because other important experiments also require the development of such techniques. The HO_2 mass accommodation coefficient is known for certain surfaces (e.g., fused silica) from laboratory experiments. As a first step, measurements could be extended to surfaces more closely similar to that of natural aerosol.

An important precursor of HO_x is formaldehyde. It is generated during the photochemical oxidation of hydrocarbons, notably CH_4 and olefins. Upon photolysis below 340 nm, it yields H atoms and HCO which react with O_2 to form HO_2. Research similar to that for H_2O_2 is required. Formaldehyde also may participate in aqueous-phase reactions.

There appears to exist a heterogeneous pathway leading to the production of OH. It proceeds via the presumably heterogeneous production of HNO_2 and appears to be first order in NO_2 (Kessler, 1984) and not to depend on NO. The mechanism is not clear, but nighttime increases in the HNO_2 concentration up to 8 ppb have been observed at the Earth's surface by long-path UV absorption. The resulting maximum HNO_2/NO_2 concentration ratio is reached shortly before sunrise and averages 3 percent. This means that even in a relatively clean environment, with NO_2 mixing ratios of 1 ppb, a HNO_2 concentration of about 10^9 cm^{-3} molecules could be reached. Since photolysis is rapid, HNO_2 would be photolyzed to OH and NO by the morning Sun in a matter of 20 minutes or so with a resulting OH production rate of 10^{+6} cm^{-3} sec^{-1}. This is a significant rate and occurs at a time when the other OH generating mechanisms are still weak.

Because the mechanism is currently unknown, it is not certain if the HNO_2 production, and thus continued OH production, continues during the daytime at the same rate as at night. However, at low insolation during winter days, HONO was also found during the daytime. Although the process is most important for more polluted areas, it appears of interest and should be understood.

Aqueous-phase reactions of OH and HO_2 may be initiated by several processes including

1. Direct uptake of the radicals from the gas phase by cloud droplets
2. Aqueous-phase photolysis of HO_x precursors, e.g., H_2O_2 or HNO_2
3. Aqueous-phase reaction of longer-lived species, e.g., O_3 or H_2O_2 to form HO_x radicals

Uptake of HO_x radicals by cloud water has been treated by Chameides and Davis (1982). The authors show that uptake, particularly of HO_2, may be quite important provided the mass accommodation for uptake is sufficiently high ($\geq 10^{-4}$). Substantial aqueous-phase production of H_2O_2 is indicated. In a further study, interaction of the HO_x by uptake of O_3 is suggested by the work of Staehelin and Hoigné (1982). Another species important to defining the free radical chemistry of pristine air is CH_3OOH. The CH_3OOH is a stable product in methane oxidation chemistry, and its formation results in the loss of HO_2 and CH_3OO. The loss of CH_3O_2 to CH_3OOH affects HCHO and NO_x chemistries as well as the HO_x cycle. The CH_3OO and CH_3OOH are expected to exhibit aqueous and heterogeneous chemistries comparable to HO_2 and H_2O_2.

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The Nitrogen (N_xO_y) Cycle

In clean air, NO is the main source species of odd nitrogen, HNO_3 is the major sink species, with NO_2 and possibly PAN serving as intermediate species. Daytime and nighttime chemistry for converting these species differ. The daytime routes are reasonably well established and occur largely in the gas phase.

The behavior of the three species in clouds differs from one another. The low solubility of NO ensures its existence almost exclusively in the gas phase. In contrast, HNO_3 is so soluble that its uptake in dilute solution may be treated as irreversible (Levine and Schwartz, 1982), and it will be present only in the liquid phase. Therefore, little useful information can be gained from its measurement inside clouds. The solubility of NO_2 is not high, so that most of it will be partitioned in the gas phase. Measurement of NO and NO_2 in interstitial air would be worthwhile. Indications that NO can be produced in electrified clouds are now appearing in the scientific literature.

Removal of NO_2 at the Earth's surface appears to be a reasonably important heterogeneous process, although there are indications that soils may also be a source of NO. Nitric acid is removed both by dry and wet deposition. An important heterogeneous process in need of further clarification is the formation of NH_4NO_3. Its importance stems not only from the neutralization of HNO_3 in the atmosphere but also from the fact that decomposition of NH_4NO_3 aerosols in a measuring instrument, or conversely the formation of NH_4NO_3 on the walls of such apparatus, can give incorrect NH_3 and HNO_3 measurements. Needed are laboratory studies on the equilibrium constants in the $NH_3/HNO_3/H_2SO_4/H_2O$ system and the rates of the forward and back reactions, including the effects of surfaces. Field measurements should include simultaneous NH_3 and HNO_3 measurements along with NH_4NO_3 particle concentrations.

Vertical flux of HNO_3 can probably be calculated with sufficient accuracy, but is probably worth measuring to test the assumptions in the micrometeorological calculations.

The set NO, NO_2, HNO_3, NO_3^-, PAN, and O_3 is a good set of candidates for field studies in clouds.

Lightning and electrified clouds are significant natural sources of fixed nitrogen; techniques for characterizing stroke and glow discharges have improved considerably, and so this fixed nitrogen source deserves further study.

Global budgets of all nitrogen sources including fossil fuel, soil release, and biomass burning should be refined. Satellite measurements could provide such information. Biomass-burning sources might also be measured on flights of opportunity.

Although perhaps not directly connected with heterogeneous processes, HNO_4 may be a significant nitrogen species at higher tropospheric altitudes and should be measured if possible during the stratospheric and tropospheric exchange mission.

Nighttime nitrogen chemistry involves NO_3 and N_2O_5, both of which participate in heterogeneous processes. Still to be determined are their mass accommodation coefficients.

Both N_2O_5 and NO_3 are good candidates for cloud studies at night and, again, because of its strong temperature dependence, N_2O_5 is a good species for measurement in the high-altitude experiment.

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Potentially important aqueous-phase reactions involve free radical NO_3 and/or N_2O_5. The NO_3 is formed by the gas-phase reaction,

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

In daylight, NO_3 is rapidly photolyzed (half-life in seconds); however, at night, NO_3 can react with a second NO_2,

$$NO_3 + NO_2 \rightarrow N_2O_5$$

to form N_2O_5. There is every reason to believe that N_2O_5 would be rapidly taken up by liquid water to form HNO_3; perhaps NO_3 also reacts directly with liquid water. Field measurements showing vanishingly low NO_3 (at night) at relative humidity exceeding about 60 percent provide support for the occurrence of this process. This process may also occur, with lower yield, if uptake of NO_3 by water is sufficiently rapid to compete with photolysis (Heikes and Thompson, 1983).

The NH_3 is probably slowly oxidized in the atmosphere, conceivably by reaction with OH. However, this process seems too slow compared with heterogeneous conversion to NH_4^+ to be of major interest.

Until a few years ago, it was widely supposed that the aqueous-phase reaction of $2NO_2$ to form $HNO_2 + HNO_3$ or of $NO + NO_2$ to form $2HNO_2$ was rapid. Lee and Schwartz (1981) showed that despite high-rate coefficients for reaction, the low solubility of these compounds severely limited the possible rates of these reactions. Nonetheless, there remain strong indications from field measurements of unknown, presumably heterogeneous reactions forming HNO_2.

Aqueous-Phase PAN Chemistry

PAN (peroxyacetyl nitrate) has been recognized as an important reservoir of gas-phase odd nitrogen. It has been suggested as well that PAN might undergo significant aqueous-phase chemistry. Recent work (Lee et al., 1983) has examined the solubility and aqueous-phase kinetics of PAN. The low solubility and first-order kinetics (Henry's law constant, $H = 4\ M\ atm^{-1}$; $k(1) = 5 \times 10^{-4}\ s^{-1}$ for pH = 4.5 to 6) would appear to rule out significant aqueous-phase reaction of PAN, at least by first-order decomposition. For a liquid-water content of 1 $cm^3\ m^{-3}$, the decomposition rate is evaluated as 0.02 percent h^{-1}.

The Sulfur Cycle

The principal anthropogenic sulfur compound is sulfur dioxide. The principal biogenic sulfur emissions appear as hydrogen sulfide and carbonyl sulfide. All three of these compounds are probably emitted in minor quantities by volcanoes of various types. Large amounts of dimethyl sulfide are emitted at the ocean surface. Lesser amounts of dimethyl disulfide, methyl mercaptan, and carbon disulfide arise from assorted natural and industrial sources.

Given time and neglecting dry deposition of the gases, it is likely that the sulfur in all these compounds is converted into sulfate. However, there are a number of sulfur species of sufficient stability that, if they are formed as intermediates,

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could reach detectable concentrations in the atmosphere. Some are known, others are claimed, still others are either found in laboratory systems or are logical precursors or successors to known compounds. Of all these, some could be important because of known or suspected biological or other impacts.

In concept, if all these suspected minor sulfur species are about equally present, probably none could reach important concentrations; the total amount of sulfur unaccounted for by transformation to sulfate is probably not more than 10 percent. However, if that 10 percent comprises a small number of compounds, there could be major consequences.

Known atmospheric sulfur species include elemental sulfur, sulfites, methanesulfonic acid, and hydroxymethane sulfonic acid. Reported species less firmly established include dimethyl sulfate, dimethyl sulfoxide and sulfone, and nitrosyl bisulfate. Reasonably expected compounds could include thiosulfates, polysulfides, polythionates, metal sulfito or sulfonato complexes, and conceivably peroxysulfates. All have some heterogeneous aspect, either being solid or liquid and/or probably formed in the aqueous (or other heterogeneous) phase. Any of these could represent emitted sulfur that did not end up as sulfate/sulfuric acid.

The species SO_2 exhibits rather high solubility in cloud water in view of the acid dissociation equilibria to form, principally, HSO_3^-, the solubility varying inversely with H^+ concentrations. Dissolved sulfur(IV) is oxidized readily by strong oxidants, notably H_2O_2 and O_3, in the atmosphere. Using laboratory kinetic data, it is possible to evaluate rates of atmospheric oxidations of SO_2 by these oxidants. Oxidation by H_2O_2 is acid catalyzed; this dependence together with the $[H^+]$-dependent solubility leads to an overall near-independence of the oxidation rate upon $[H^+]$ in the pH range of 2 to 6. The oxidation rate evaluated for 1 ppb H_2O_2 at a liquid-water content of 1 cm^3 m^{-3} is approximately 500 percent hr^{-1}. The rate of reaction of S(IV) with O_3 increases somewhat with decreasing $[H^+]$ leading to an overall rather strong $[H^+]$ dependence of the oxidation rate referred to gaseous reagents, increasing with increasing pH. At pH 6, the oxidation rate of SO_2 for 30 ppb O_3 and 1 cm^3 m^{-3} liquid-water content is approximately the same as that for 1 ppb H_2O_2; however, at pH 3, the rate is approximately 4 orders of magnitude lower than that of the H_2O_2 reaction.

The importance of catalyzed O_2 oxidation to atmospheric oxidation of SO_2 is less clearly established. Transition-metal-ion catalysis is thought perhaps to be important for iron and/or manganese concentrations of the order of 10^{-6} M, but such concentrations would be uncommon; oxidation by suspended particulate carbon has received much attention. Evidently, laboratory (as well as ambient) rates depend sensitively on the physical state of the carbon catalyst. Recently Harrison and Pio (1983) have questioned the importance of carbon-catalyzed SO_2 oxidation in the atmosphere.

Few field data are available on SO_2 oxidation. Rather, rapid oxidation rates (up to ~2000 percent h^{-1}) have been reported by Hegg and Hobbs (1981, 1982), although the interpretation of these studies has been questioned (Schwartz and Newman, 1983). There is, as well, considerable inferential information based on cloud composition measurements (Daum et al., 1983, 1984; and Ferek et al., 1983).

The rate constants for the reactions between organic peroxides and dissolved SO_2 species have recently been measured. Methyl hydroperoxide (CH_3OOH) reacts at nearly one-fourth the rate of H_2O_2 and shows an identical pH dependence. Tropospheric CH_3OOH has not been measured, but is estimated to be between 30 to 100 percent of the

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H_2O_2 concentration when NO_x is low, <100 pptv (Calvert and Stockwell, 1983; Thompson and Cicerone, 1982). At these levels and rates, CH_3OOH is potentially a major unquantified oxidant in the aqueous-sulfur cycle. Current research demonstrates that peracetic acid (CH_3COO_2H) can also lead to appreciable aqueous-conversion rates of SO_2 to sulfate and that it would be present in pristine air at levels dependent upon PAN, HO, and NO_x.

The Carbon Cycle

Though a large number of carbon compounds are known to occur in polluted atmospheres, only a few appear to be of major importance in heterogeneous atmospheric chemistry. Elemental carbon is a major suspect for a role as a catalytic material in heterogeneous reactions of other species, but carbon itself is not a reactant of consequence. Inorganic carbonates appear to react with sulfur and perhaps nitrogen oxides, but this is not an important sink for these species under most conditions. The facile reaction of benzo (a) pyrene sorbed on carbon with NO_2 to yield nitrobenzpyrenes, some of which are potent mutagens, has obvious biological significance, but it has little role in the global budget of either carbon or nitrogen.

Probably only two groups of compounds qualify for consideration in this context. The first group is the one- and two-carbon aldehydes and carboxylic acids. The acids were probably first identified in particulate matter in the 1950's and found later to comprise a significant fraction of precipitation acidity. Acetaldehyde and formaldehyde are found in air and are almost certainly the precursors of the carboxylic acids through an aqueous-phase reaction. Also, formaldehyde, and possibly other aldehydes, stabilize S(IV) by complex formation inhibiting its oxidation and sulfate.

The other group of organic compounds is less well characterized. This group is composed of high-molecular-weight polar compounds, some probably primary plant waxes, and partial-oxidation products of terpenes and petroleum products, which are surface active and form layers on aqueous droplets and aerosols. While it appears unlikely that there will often be sufficient time for such films to form on growing droplets, they could have considerable importance on evaporating droplets and particles. Despite the possible profound consequences of these in terms of retarded evaporation of clouds and fogs and modification of rates of heterogeneous reactions, very little is known about them, although they are now the subject of research in both the U.S. and Japan.

The Halogen Cycle

The halogen family of elements, particularly Cl, Br, and I, has a set of rather unique properties with respect to heterogeneous atmospheric chemistry. Halogen-containing species are found in gaseous, aerosol, and aqueous phases in several oxidation states which are relatively easily and rapidly interconvertible. Information about halide concentrations and concentration ratios to each other and to Na, not only below but also in and above tall convective clouds over a marine environment, could be very helpful in determining physicochemical conditions in the cloud and in better understanding the chemical processing of the more important N, S, and C species. It could also be helpful in understanding long-range transport of halogens in the upper troposphere, their possible participation in photochemical/ homogeneous atmospheric chemistry, and their abundances and relative concentrations in remote planetary regions.

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Sea-salt particulates, containing halides, are normally found in a well-mixed boundary layer. They are formed by droplet ejection from bursting bubbles at the sea surface, followed by evaporative shrinkage to a minimum size determined by the amount of salt and humidity, and the amount of organic surface coating. The particles are then mixed within the turbulent boundary layer, and may later serve as cloud condensation nuclei and be chemically processed and transported within clouds. They can then be ejected into the air above an evaporating cloud as a chemically new species of gases or aerosol residue, or they can be recycled downwards. Horizontal transportation in any phase is also possible. The field experiment envisioned would sample the various parts of this cycle, in conjunction with the study of the chemistry and transport of other important species in tall convective clouds in a marine environment.

Chemically, the Cl, Br, and I are initially in the -1 (ionic) oxidation state; I is also in the +5 state as IO_3^-. Both Cl and Br can be oxidized to the zero (elemental) state and further to positive oxyacid states. In the -1 state, they exist either as nonvolatile salts (MeX) or volatile hydroacids (HX). The free elements are all volatile, as are the lower oxyacids, which tend to decompose to the gaseous products, HX and X_2. Ease of oxidation is in the order I > Br > Cl.

In clouds that are acidic because of the nonvolatile sulfuric acid, HX and X_2 will be produced and ejected into the gaseous phase by evaporating cloud droplets. The relative amount of X_2 to HX for each of the halogens, and the ratios of I to Br to Cl above the cloud compared to the same ratios for the salts below the cloud, could be used to obtain information useful in understanding oxidation rates for other reduced species of, for example, sulfur and nitrogen in evaporating clouds.

Oxidation of the halide to free halogen is perhaps accomplished primarily by photochemistry; the I^- is oxidized the most readily. Day and night variations of the ratios of gaseous and particulate halides among each other, for various particle sizes, and at various altitudes outside of clouds might be useful in interpretation of photochemical conditions important to reactions of other chemical species.

Since organics, especially methyl-halides, also make up a large fraction of the total halogen in the atmosphere, they must also be measured and considered in any experiment. They are most likely to be of importance in photochemistry, however, and will perhaps not be significant in cloud experiments.

FIELD STUDIES (AQUEOUS PHASE)

At the present time, there is a serious need for new field data to directly confirm the occurrence and quantify the rate of in-cloud aqueous-phase reactions. In large part this is due to the absence of appropriate instrumentation. However, to a major extent this reflects the complexity of transport processes of clouds that make the direct unambiguous study of reactions in clouds a very difficult endeavor.

In view of these considerations, a deliberate, staged series of investigations is recommended, proceeding forward only on the basis of established and documented capabilities. These capabilities include, in the first instance, the ability to measure desired species in or out of clouds with the necessary time resolution. Considerable insight may be gained simply by documenting concentrations of pertinent species within clouds and the dependence of such concentrations on other conditions, such as pre-cloud concentrations, solar intensity, and type of cloud, etc. In such studies, the use of tracers to mark pre-cloud air and document air flows will be of

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considerable utility. First-cut evaluations of the importance of particular processes may be gained by evaluating kinetic rates making use of laboratory data. Additionally, considerable insight may be gained by examination of concentrations in relation to pre-cloud concentrations (depletion of reagents or buildup of products) which will provide support for or against the occurrence of particular reactions. Such studies should be conducted in a variety of locations and may be suitably conducted in conjunction with other projects in the GTE (Global Tropospheric Experiment).

A second stage of studies would logically be an attempt to determine kinetic rates in well-defined model-cloud systems. Two possibilities are suggested here. The first is measurement of time evolution of concentrations in a steady-state cloud. Here, ground measurements in fog in the absence of advection might be suitable. Appropriate attention must be paid to documentation of material losses, e.g., by droplet deposition. A second class of experiments is studied in wave clouds.

Looking beyond this second stage of field studies, a variety of possible studies is envisioned in increasingly complex cloud systems: single cumulus and cloud streets associated with roll circulation, etc. At the present time, however, it is premature to undertake kinetic studies in such systems, although documentation of concentrations of pertinent species, as described previously, would be quite useful.

Near-Term Studies

A comprehensive study of cloud chemistry will require a large set of measurements, a set likely not within realistic current capabilities. We therefore propose a stepped approach to a cloud sampling project, beginning with small field intercalibration experiments and cloud chemistry studies involving a limited set of measurements.

For the near term, a number of options for a cloud sampling project are recommended. The project should be initiated with a field intercalibration of selected instruments; the intercalibration might be carried out as a "flight of opportunity" or "piggy back" experiment on a NASA GTE flight to the remote Pacific. Following successful intercalibration, a dedicated field experiment to study cloud systems is suggested. Depending upon technology availability, three possible options for this field experiment are recommended. These options are listed in order of increasing complexity.

Option "1" - (H_xO_y Experiment)

- O_3, H_2O, OH, H_2O_2, and CO in gas phase
- H_2O_2, H^+, and carbon and metal catalysts in cloud water
- O_3 photolysis rate
- Temperature, liquid-water content, ice concentration, and organic acids

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Option "2" - (Daytime N Experiment)

- Option "1" plus NO, NO_2, HNO_3, and NH_3 in gas phase
- NO_3^-, NH_4^+, and H^+ in cloud water and particles

Option "3" - (S Experiment)

- Option "1" plus SO_2, HCHO, organic peroxides, and dimethyl sulfide (DMS) in gas phase
- S(IV), $SO_4^=$, transition metals, particulate C, and NH_4^+ in cloud water and particles

In practice it may be possible and effective to the objectives of the overall project to carry out the several options simultaneously.

Wave Clouds

It appears desirable to study aqueous-phase transformation processes under the natural conditions of a real cloud or cloud system. During the workshop, several types of clouds were proposed for conduct of such studies: streets of clouds in the marine and continental boundary layer, wave clouds, extended stratus in the marine boundary layer, and single, small, or large cumulus clouds in maritime and continental environments. The basic concept of the experiment is to balance the input and output of a gaseous precursor against the input and output of the heterogeneously generated product (for example, conversion of NO_2 to HNO_3 and nitrate aerosol). This requires sampling the clear air at the inflow and outflow regime of the cloud, and thus requires precise identification of the location of these regimes.

In the less turbulent clouds, these measurements should be augmented by in-cloud measurements of crucial reaction species in the gas and aqueous phase. Because they present the simplest and smoothest flow, wave clouds should be the first to be studied. In fact, studies of this type, although less complete, have already been made by Hegg and Hobbs (1981, 1982, and 1983). Depending on the transit times through the clouds, various types of chemical cycles can be studied: the conversion chain $NO_2 \rightarrow NO_3 \rightarrow N_2O_5 \rightarrow HNO_3(aq) \rightarrow$ nitrate aerosol, the conversion of SO_2 to sulfate aerosol, and the conversion of CH_2O to HCOOH and possibly further to CO. Day and nighttime experiments are needed. The final goal would be to obtain conversion rates, and, if some of the reactants like H_2O_2 can be measured inside the cloud, to infer the nature of the key reactions.

Not all the techniques for these experiments are ready, and instrument development is required (see tables I through XXI, National Academy of Sciences (1984)).

This experiment would benefit greatly from collection and analysis of cloud water. It would be desirable to utilize a suitable tracer (e.g., SF_6) to trace the air flow.

For the H_2CO conversion, not enough is known about its tropospheric distribution to specify necessary detection limits.

Obviously, substantial instrument development and field testing are required for all these experiments and are all that can probably be expected in the near term.

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Single-Cloud Cumulus

In order to understand the transport and transformation processes in cumulus clouds, single-cloud measurements should focus on small cumulus (nonprecipitating, vertical extent <3 km) and isolated cumulonimbus (rain producing) clouds to determine the modification produced in the local cloud environment and to observe directly the chemical transformation occurring in the cloud water. Care must be taken to select the optimum meteorological conditions for each experiment to simplify the logistical problems, to reduce potential ambiguities, and to assure representative sampling. Because these convective elements are so complicated in structure and involve such a broad spectrum of microphysical processes and cumulus scale circulations, it is important that cloud modeling efforts be integrated into the field measurement program. It is unlikely that a sufficient number of physical, dynamical, and chemical measurements can ever be made to resolve for any single cloud all the transport and transformation processes without the aid of a chemical cloud model to interpret the field measurements. In order to be as mechanistic as possible and to reduce the number of processes that must be parameterized, it seems appropriate to use a fully three-dimensional, numerical model. Models with lower dimensionalities would require greater parameterizations and are not as likely to be able to incorporate the data from the field measurements. The aircraft sampling should be conducted from the initial stages of cloud development through the dissipation of the cloud so that the modification of the vertical distributions of trace substances in the cloud environment can be determined. Boundary layer updraft and downdraft air should be sampled as well as the air adjacent to the sides of the cloud because entrainment of air through the sides may be as large as through the cloud base. Turbulent flux measurements, both vertical and horizontal, should be made to estimate the cloud entrainment. Doppler radar should be used to map the three-dimensional motion field within the cloud and to estimate the cloud liquid-water content. Air detrained at or near the cloud top should also be sampled. A key part of the experiment should be to measure the redistribution of trace substances produced by the cloud following its dissipation.

Penetrations of the cloud at several levels should be made to collect cloud water and sample the institial air. These measurements need not be made to resolve fully the three-dimensional distribution of chemical substances in the cloud air and water, but rather to provide some validation for the cloud microphysical and chemical model.

Based on our current understanding of cloud chemistry, it is desirable that simultaneous measurement capabilities under cloud conditions for the following be developed and verified:

1. Gas phase: O_3, NO, NO_2, NO_3, HNO_3, SO_2, OH, H_2O_2, NH_3, RCHO, RCOOH, and HX
2. Aqueous phase: H^+, $SO_4^=$, NO_3^-, $RCOO^-$, HSO_3^-, NH_4^+, H_2O_2, H_2CO, S(IV), and X^-
3. Physical parameters: temperature, solar flux, liquid-water content for warm, supercooled, and glaciated clouds, and droplet size distribution

The instrument requirements for this experiment are generally the same as for the wave cloud experiment.

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Long-Range Transport

Our present ability to calculate the movement and dispersion of air masses on a global scale is, in general, quite poor, especially over oceans, where meteorological data are very sparse. Vertical transport with possible simultaneous chemical transformation of chemical species occurring via clouds may be very important, but it is also quite poorly understood.

Over the past several years, atmospheric scientists have begun to use characteristic physical and chemical properties of particles from certain regions to identify air masses and to observe their long-range transport from those regions. Perhaps the earliest example of the use of such tracers was the observation of Saharan dust across the Atlantic Ocean (Carlson and Prospero, 1972). Rahn (1981) used the ratio of noncrustal Mn to that of V of particles in the Arctic atmosphere to identify the major source of the particles as Eurasia. More recently, Rahn and Lowenthal (1984) developed a set of elemental tracers based on the ratios of the particle-borne concentrations of Zn, As, Sb, In, and noncrustal V and Mn to the concentration of particulate Se. They find that the pattern of these ratios is quite different for particles from six regions of the world that have been investigated: Interior U.S., East Coast U.S., Southern Ontario, Eastern Canada, Eastern Europe, and Western Europe. As a part of that work, one of their most remarkable findings was the observation of particles from Canadian smelters at their sampling site at Narragansett, RI (Rahn et al., 1983). These particles are distinguished mainly by their usually large In/Se ratios. Although the seven-element tracer system is promising, it will surely be possible to develop more definitive tracers by investigation of many more species. Also, the tracer criteria for some of the regions were based on the analysis of very few samples.

Since February 1979, Parrington and Zoller (1983) have been determining detailed concentration patterns (of about 40 elements) of atmospheric particles collected on a weekly basis at Mauna Loa Observatory (MLO) on the island of Hawaii. The MLO is located at 3400 m altitude, i.e., above the boundary layer. A sample controller was used to collect downslope samples at night and upslope samples during the day. The former is thought to be representative of air at about 4 km height, and the latter is thought to be representative of air at about 2 km height, also including some material from the island itself and the sea.

The most interesting result of the MLO studies is the observation of a very large influx of Asian dust every spring, from about March to June, also observed by Duce et al. (1983) at the Enewetak Atoll. This dust, probably originating from deserts in China, has a composition quite different from that of Hawaiian soil, so it can easily be distinguished. During an 8-week period in spring 1980, another type of Asian dust with a different composition was observed, presumably from a different source area in Asia. Ten-day back trajectories for selected sampling periods were calculated by the NOAA Global Monitoring for Climatic Changes (GMCC) group (Harris, 1982) and, while they do indicate an origin somewhere in the vicinity of China, they are much too crude to pinpoint the locations. The understanding of these long-range transport situations could be greatly enhanced if the air masses bearing high dust loadings could be tracked from their origins in Asia and across the ocean to the points at which the dust is observed at MLO, Enewetak, or in the Arctic (Rahn et al., 1981). Satellite observations have been used for tracking the Saharan dust cloud (Prospero, 1981) and can be very useful for additional work of this nature.

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Many other types of particles are observable at MLO. During nondust periods, the predominant species in terms of mass of particulates is sulfate. The concentration of sulfate (as well as of the chemically similar Se) has a broad seasonal maximum that peaks in late May or early June, which suggests a biological origin for the sulfur, presumably as a gas, a portion of which is transformed to sulfate particles by atmospheric processes. Superimposed upon this general sulfate background are frequent short-term increases in sulfate concentration ("spikes"), often accompanied by similar concentration spikes for various trace elements such as V, Sb, Zn, Cu, and even W and In. These enhanced trace element concentrations are characteristic of high-temperature processes such as ore smelting or combustion of fossil fuels, or of natural high-temperature processes that occur in volcanoes. Back trajectories have been computed for some of these "spike" events, many of which appear to originate in Asia, but some very strong ones appear to come from Mexico and Central America. One of the most interesting of the spikes has an elemental concentration pattern characteristic of copper smelters and the back trajectories suggest an origin in the Southwestern United States. This result, including the observation of a spike for the rare element, indium, is in agreement with the observation of particles from Canadian smelters at Narragansett, RI, by Rahn et al. (1983). As yet, clear evidence of spikes resulting from volcanoes has not been observed in the MLO data set, except for local perturbations caused by emissions from Kilauea on the island itself. It would be quite useful for testing and improving trajectory calculations if the origins of these events could be determined from satellites. The particles bearing sulfates and trace elements are predominantly of sizes appropriate for scattering and absorption of visible light throughout their residence times in the atmosphere. It would be especially valuable if particles from a "pulsed" event, e.g., a volcanic eruption, could be observed because one would know not only the atmospheric path of the material but also the times at which the material was released and picked up at the sampling site.

Much has been learned by applications of receptor model techniques, especially chemical element balances (CEBs) and factor analysis. For example, the sources of particulate sulfur (mostly as sulfate) were estimated. Of the yearly average concentration of about 165 ng/m^3 of S, about 70 ng/m^3 are associated with episodic spikes (mostly from anthropogenic activities, but perhaps some from volcanic) and about 30 ng/m^3 from seasonal marine activity (probably associated with biological activity in the ocean), with a broad peak centered in May. Underlying these variable concentrations is a constant, global background of about 65 ng/m^3 that is observed at many clean sites, including the South Pole. The source(s) of this background sulfur is not known, but it probably comes in comparable amounts from biological activity and anthropogenic activities, with some volcanic input and input from stratospheric OCS.

Upslope samples at MLO carry marine aerosol as shown by the presence of Na, K, Ca, and Mg, etc., but downslope samples show very little of it, probably because sea salt is so soluble that its movement up the 4-km level is blocked by cloud processes and washout. On the other hand, particles bearing Br and I, whose ultimate source is surely the sea, have almost identical concentrations in upslope and downslope air. The explanation is that I and Br probably go through the gas phase, perhaps as organic halides. If so, these gases may be so insoluble as to not be affected by cloud processes. If these hypotheses could be verified (e.g., by measuring organic halide gases), one could use the results to gain some understanding of the effects of clouds on vertical transport.

The MLO data provide crude information on vertical profiles of elemental concentrations, but far more data are needed if we are to use the information to gain an understanding of vertical transport and the factors that govern it, e.g., phase

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changes, solubility, and particle size, etc. Very few data now exist on vertical profiles of elements borne by particles and trace gases. The only explicit study was that reported by Gillette and Blifford (1971). Recently, Phelan (1983) collected background particles from NASA aircraft during flights from their bases to sites of volcanoes that were studied, and analyzed the particles for a substantial number of elements. Her work showed the potential value of such collections and analyses, but a great deal more needs to be done.

Satellite Observations

Haze, Fog, and Stratus

Some of the characteristics of haze, fog, and stratus can be measured by the radiance of scattered sunlight with radiometers carried by geostationary and polar-orbiting satellites. The observations are made every half hour and daily by the geostationary and polar-orbiting satellites, respectively, with a spatial resolution of 4 km. The boundaries of stratus and dense fog can be delineated. From the contours of radiance over light fog and haze, their particulate surface area and mass can be derived from empirical or model data on the relations between their physical and optical characteristics (R. S. Fraser, NASA Goddard, work in progress). Such a procedure still requires validation with independent measurements, which can be acquired during aircraft observations supporting an experiment.

Ghost Clouds

Ghost clouds, or locally high concentrations of clear-air aerosols, are invisible to the eye but are evident from reduced solar transmission in atmospheres with a very low aerosol optical thickness. Their presence at the Mauna Loa Observatory, where the background aerosol optical thickness is 0.02, is evidenced by a sudden reduction in sunlight. Particles with diameters of a few hundredths of a micrometer, which have a negligible effect on solar transmission, become agglomerated into optically effective particles that are an order of magnitude larger. Since the ghost clouds are invisible to the eye, their optical thickness would seem to be less than a few hundredths. Satellites cannot detect regions of high aerosol concentrations over the ocean unless their optical thickness exceeds 0.05. Hence, satellites would not be expected to detect the ghost clouds.

Tracers

Dense dust storms can be detected by satellites in their source region and followed for several thousand kilometers over the sea (Otterman et al., 1982; Carlson, 1979). The most useful satellite radiometers for following the dust within the next few years are carried by the geostationary and polar-orbiting satellites NOAA-7 and -8, which are operating now. Each point on the Earth is observed once during each day and also at night by the polar-orbiting satellites, with a spatial resolution of a few kilometers. If the optical thickness of the dust in the visible spectrum exceeds 0.05, it can be measured in the daytime over the ocean with an accuracy of 0.05. The capability of deriving particle surface area and mass needs further development.

The satellite data do not provide useful height information; the dust diffuses horizontally. If a branch of dust diverges from the main body, its height may possibly be determined by knowledge of the wind that carries the dust.

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Regional-Scale Redistributions

The redistribution of trace substances by clouds can be most directly addressed by measurements in single-cloud experiments. The larger scale impact of this redistribution by individual clouds, although much more difficult to evaluate with a field measurement program, needs to be addressed. This redistribution process is important for the gas-phase trace substances, particularly odd nitrogen, ozone, odd hydrogen, and sulfur compounds, and for aqueous-phase chemistry because it affects the in-cloud scavenging processes and also the levels of detrainment of cloud-processed gases and aerosols.

Several groups have made significant contributions to the interaction of cloud transport to air chemistry on the synoptic scale. Ching (1982) has shown the sensitivity of the regional oxidant buildup process to cloud venting, resulting in the net removal of ozone from the boundary layer. Greenhut et al. (1982) have examined a case study of this venting process and discussed its importance in modifying the local cloud environment. Scott (1982) has presented two microphysical models, in which individual systems interact with their environment in summertime (convective) and wintertime (stable cyclonic) storms, using simple models of the updraft and downdraft structure. Hong and Carmichael (1982) have described the interaction of a small cloud's aqueous-phase chemistry with a cloud model using prescribed transport through the cloud. Gidel (1983) has considered the cloud transport of tracers of various lifetimes and finds their inclusion to be potentially significant for the ozone and nitrogen budgets. Chatfield (1982) has constructed a model of the tropospheric transport and photochemistry of SO_2 in tropical systems and finds vertical distributions of SO_2 different from those of diffusion models.

There are two approaches to making the kind of measurements which are needed to validate and test the significance of the cloud transport processes discussed in these models. One is to extrapolate the redistribution due to single clouds by accounting for the number and size of clouds within the region: mesoscale, synoptic scale, and global scale. This effort may make use of the global cloud climatology which is being produced by the International Satellite Cloud Climatology Project (ISCCP). Measurements of the redistribution of trace substances by individual clouds are discussed in more detail in the section, Single-Cloud Cumulus. However, in essence, it involves making vertical profile measurements in the local air where the cloud formed, both before and after the cloud has dissipated, and from the profiles, extracting the changes which occurred on the timescale of the lifetime of the cloud. This should be done for soluble and insoluble trace substances in order to assess the gross wet removal, particularly for the most soluble gaseous species such as HNO_3, HCl, and H_2O_2. Substances with a variety of gas-phase lifetimes should be considered. Radioactive isotopes would also be useful tracers for this purpose. Measurement systems, such as the ultraviolet differential absorption lidar (UV-DIAL) which can measure ozone, aerosols, and SO_2 in high concentrations, appear to be ideally suited for these experiments because of their ability to make profiles quickly and often and to look vertically, which may be useful for obtaining profiles in the environment of tall cumulonimbus clouds. The disadvantages of this kind of experiment are that it is difficult to produce a budget for a single cloud and that there are uncertainties associated with the extrapolation of measurements from single clouds to the entire ensemble of clouds in a mesoscale or synoptic region.

The second approach to evaluating the regional-scale impact of cloud vertical redistribution involves making vertical profile measurements over a much broader spatial scale (100 to 500 km) in cloud-free air in a region embedded with numerous convective elements. From these measurements, the regional-scale trace substance

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budgets could be diagnostically evaluated to determine the area-averaged cloud fluxes of whatever trace substance profiles are measured. Appropriate tracers need to be selected for release on existing substances with known source and source strength. These regional budget studies also require measurements of wind, temperature, moisture, and solar radiation in order to diagnose the cloud mass fluxes from the meteorological heat and moisture budgets. From an array of stations (typically 5 to 10 in number), 3-hour serial vertical soundings of wind, temperature, and water vapor are made. From the heat and moisture budgets for the region (100 to 500 km spatial scale), it is possible to diagnose the cloud mass fluxes based on the soundings at each of the release points. The time tendency terms and the large-scale advective transports can be calculated from the sounding information. Then using the area average cloud mass fluxes determined from the meteorological budgets, the trace gas budgets can be evaluated, since both the large-scale tracer transports and the cloud transports can be calculated from the tracer soundings at each of the release points.

The cloud mass fluxes determined from the heat and moisture budgets would be applicable to all other trace constituent budgets, but it would be desirable to carefully choose tracers with characteristically different photochemical behaviors. Species such as O_3, CO, and NO_x would be good choices as insoluble gases and would enable calculation of OH. In addition, SO_2, H_2O_2, HNO_3, HCl, and/or aerosols would be good choices for soluble constituents. It would be necessary to make vertical profiles of these constituents in cloud-free air between the ground and the upper troposphere or at least to the top of the cloud layer.

However, because this is a formidable field experiment, it may not be tactically feasible in the near term. In this case, a more severely truncated experiment should be considered with only one trace species such as ozone. Measurement systems such as ozonesondes and the UV-DIAL system already exist for making vertical-profile measurements, and the whole chemistry part of the field experiment could be "piggy backed" on a number of proposed or existing meteorological experiments which use serial ascents of arrays of rawinsonde balloons. This would provide some evaluation of the role of fast cloud transport processes on the meso- and/or synoptic scale, and would provide some verification for regional- and global-scale models that are attempting to incorporate these processes.

An Experiment of Opportunity

Available evidence suggests two routes for the transformation of sulfur dioxide into sulfate. In one, chemical transformations occur in the gaseous phase, with only the end product leading to particle formation or growth. In the other, the sulfur dioxide molecule dissolves in or deposits on a droplet or particle, after which oxidation to sulfate occurs. The former route is photochemical; the latter is probably not. Among evidence for the latter route is the rapid conversion of sulfur dioxide during acute pollution episodes in London during the 1940's and 1950's, during fogs so dense as to require street lights at midday. Photochemical processes were thus poor candidates to account for sulfur dioxide lifetimes of a few hours.

Insight into the relative contributions of the two routes can be gained by measurements of sulfur dioxide, sulfate, ammonia, ammonium, hydrogen peroxide, and trace metals, etc., in relatively polluted fogs and hazes in the surface mixing layer. While this study will also contribute to the understanding of local pollution problems, it is viewed here rather as an effort to clarify and flesh out understanding of the sulfur budget.

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The study might begin with a survey of old data from London. It could probably then be viewed as an experiment of opportunity attached to other fog, haze, or cloud studies. Measurement sensitivity requirements would be easily met, since the best sites for measurement would be relatively polluted ones. Several sets of measurements are needed to give information as to which potential oxidizing or catalytic agents correlate with the degree of sulfate conversion.

Marine Boundary Layer Experiment

The marine boundary layer (MBL) is the thermodynamically well-mixed layer of the atmosphere overlying the ocean surface. In undisturbed or suppressed weather conditions, its thickness depends on the sea surface temperatures and is typically 50 mb to 75 mb (500 m to 750 m). Clouds that often cap the MBL can significantly modify the thermodynamic and chemical structures. Observational studies during GATE (Global Atlantic Tropical Experiment) found that some clouds tend to cool and dry the MBL, others tend to warm and moisten it, while still others tend to warm and dry it (Emmitt, 1978). Cloud updrafts and downdrafts often extend far below the cloud base and are traceable to near the ocean surface as perturbations in vertical velocity, temperature, and specific humidity. The clouds that cap the MBL can also modify the liquid-water content of the mixed layer through drizzle. Occasionally, the clouds above the MBL are roughly organized into ordered rows or "streets." The spacing of the rows is of the order of the thickness of the mixed layer itself, and the streets may run for hundreds of kilometers. These clouds greatly enhance the entrainment of free tropospheric air into the MBL. The existence of alternate streets of cloud and cloud-free rows, which can persist for times measured in hours, presents an opportunity for studying fundamental processes in heterogeneous chemical cycles in air which may be going through alternate wet and dry cycles. Streamlines for this roll vortex situation are actually more complex than indicated by this simplified description and by the diagram in figure 10, so sampling patterns will have to be carefully designed with this in mind.

Some of the goals of a marine boundary layer study are

1. To determine the sulfur budget of the marine environment and the contribution of marine sulfur to the free troposphere

2. To study the origin, properties, and chemical transformation of sulfate and salt particles in the MBL, including halogen chemistry

3. To analyze the heterogeneous nitrogen chemistry of marine aerosols and clouds

4. To characterize organic compounds in the marine environment

Figure 10 shows two possible measurement strategies in the MBL. The first corresponds to common MBL conditions in which sampling can be conducted below, in, and above the marine stratus. Long, straight flight paths and extended sampling times are possible. The second panel of figure 10 illustrates a less common but potentially interesting MBL condition where rolling convection produces cap clouds. Here, sampling could be designed to intercept air parcels before and after cloud processing. However, the sampling times would be limited to perhaps 5 min or less (longer sampling times could be achieved by flying parallel to the convective cells, and down the streets). In either situation illustrated in figure 10, shipboard vessels could be positioned to provide supporting data on a long time scale.

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One possible experimental plan is outlined in table XXII. The measurements listed are a complement to the high-priority measurements carried on the GTE aircraft (e.g., OH, NO, NO_2, and O_3) as well as the standard meteorological data collected on such missions. It is also possible to trace aerosols and winds using the DIAL lidar system, which would have to be carried on a second dedicated aircraft. Some of the experiments could be stationed aboard boats (e.g., instruments for DMS and aerosol samplers) to provide a more accurate data base, and independent experiments could be fielded to study air-to-ocean fluxes, which affect the overall marine budgets. In this regard, gas fluxes could be estimated using chemical analysis of surface water columns by well-developed techniques, and diurnal effects could be observed.

Table XXII is divided into distinct subsections, or experimental modules, which may be combined in different ways to achieve specific scientific objectives. Each module represents a key segment of a chemical cycle, but is most useful in combination with other modules. The experimental modules are designed to determine roughly the overall chemical budgets and transformation pathways in the marine environment. Even this rather modest goal represents a major advancement in understanding chemical budgets through coordinated observations.

To achieve this goal, measurements assigned priority A within each module are deemed essential. Measurements of priority B provide important, but not necessarily essential, supporting data. Thus, for example, an informative and unique study of the marine sulfur cycle could be constructed from the six experiments of class A listed in modules one through three.

It should be noted that overlap exists between the experimental modules which apply to different chemical cycles. Thus, aerosol and cloud water samples collected for sulfate analysis can also reveal nitrate, ammonium, carbon, and other key compounds. It follows that the addition of an experimental module would not generally require the full resources indicated for that module. It is also important to keep in mind that complementary instrument platforms, such as ships, islands, or satellites, might be profitably utilized in these field programs.

At the present time, not all of the measurements suggested in table XXII could be carried out with sufficient sensitivity, given the time constraints of an aircraft mission (although basing them on sea-going vessels could extend certain measurement times considerably). The characteristics of existing instrumentation, the technology achievements required to improve experimental capabilities, the laboratory data needed to support field and technology studies, and the modeling requirements for data analysis and interpretation are discussed.

Studies of Heterogeneous Processes in Emissions From Biomass Burning

Biomass burning is hypothesized to be an important source of many trace species of C, N, Cl, and S to the troposphere (e.g., see Crutzen et al., 1979; and Logan, 1983). Existing estimates of emissions to the troposphere from biomass burning have extrapolated a limited set of laboratory and/or field measurements (in combination with very uncertain estimates of the type and quantity of biomass burned annually) to a global estimate. Uncertainties in these calculations could easily reach a factor of 5 to 10. Because current estimates, albeit highly uncertain, indicate a potential role for biomass burning as a major source of NO_x, C_2-C_5 hydrocarbons, methyl chloride, CO, OCS, and other gaseous and particulate species, it is critically necessary to improve our understanding of processes determining both the production and dispersion of gases and particles during burning.

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It is well known from available laboratory studies and basic principles of combustion science that variables such as fuel type and combustion temperature are critical in determining combustion products. In addition, as particulate and gaseous combustion products are dispersed into the troposphere, processes such as gas-to-particle conversion, particle coagulation, gaseous adsorption and reaction on particle surfaces, and particle nucleation can modify the composition of emissions. To assess properly the importance of biomass burning in global tropospheric chemistry, a systematic long-range program of field measurements is required which includes: (1) determination of emission factors for gaseous and particulate species produced by major types of biomass burning (e.g., controlled agricultural burning, tropical land clearing, and forest fires, etc.) and (2) studies of how heterogeneous processes modify the composition of biomass-burning emissions during dispersion in the boundary layer and into the free troposphere. We propose that combined ground and aircraft measurements over controlled and uncontrolled burns can reduce much of the uncertainty related to the role of fire in global tropospheric chemistry. These studies should be conducted jointly with other agencies such as the U.S. Forest Service.

Measurement Needs

Field studies of biomass burning should attempt to measure a sufficient number of gaseous and particulate species of C, N, Cl, and S to construct an accurate mass balance of the combustion process. In addition, studies of heterogeneous processes in emission plumes will require detailed and accurate data on particle size distributions and chemistry along temperature and chemical concentration gradients within dispersion plumes. Measurement of K/Fe and C^{14}/C^{12} ratios would be useful as tracers. We recommend these specific measurements for an initial 2-year study of emissions from biomass burning.

1. Ground-based measurements should include fuel composition (C, N, Cl, S, and H_2O), burn conditions (rate, temperature, and meteorology), residue composition (C, N, Cl, S, and ash as metal oxides), smoke composition (CO_2, CO, NO_x, PAN, CH_4, SO_2, OCS, elemental C, C_2-C_5 hydrocarbons, Cl^-, CH_3Cl, and particle size), and primary oxidants K/Fe and C^{14}/C^{12}.

2. Aircraft measurements should include particle size, elemental C, Cl^-, C_2-C_5 hydrocarbons, CO_2, CO, CH_4, CH_3Cl, NO_x, PAN, SO_2, OCS, K/Fe, and C^{14}/C^{12}. The UV-DIAL should be used to determine the structure of the smoke plume to guide in situ sampling. The aircraft should have all measurements, including meteorological parameters, keyed to a universal clock to aid in subsequent data analysis.

Study Sites

There are two recommended sites for initial studies, the Southeastern United States and Brazil.

1. The Southeastern United States is the region subject to widespread controlled burning each year for agricultural and forestry management. Two significant fire research programs are located in this region, the Tall Timbers Research Station near Tallahassee, Florida, and the U.S. Forest Service Laboratory at Macon, Georgia. Collaboration with these laboratories would provide many of the ground-based data necessary for a quantitative biomass-burning study. Aircraft measurements in this region can also be easily supported by existing extensive meteorological stations. The primary disadvantage of studies in this region is the presence of other anthropogenic

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sources which can be expected to mix with biomass-burning emissions. This region is viewed as an ideal area for preliminary studies where the emphasis is on development of aircraft measurement techniques and sampling procedures.

2. It is generally agreed that a significant fraction of the world's biomass burning takes place in the tropics during land clearing and agricultural practice. Fuel types and burning conditions in the tropics will be highly variable and quite different from burning in the Southeastern U.S. We recommend that following the development of appropriate measurement and sampling techniques, a series of expeditions should be planned for studies of biomass burning in the tropics. Brazil offers a wide range of habitats which are subject to burning during the dry season (e.g., Savannah and the tropical forest). Studies of these sites will be difficult due to limited meteorological and ground-based support measurements. Aircraft measurements of heterogeneous processes in smoke plumes may be easier to execute in the tropics where other anthropogenic sources are relatively few in number.

Additional Flights of Opportunity

Many existing research programs routinely plan scientific aircraft flights in the troposphere. These flights provide an opportunity to test, develop, calibrate, and intercompare instruments for heterogeneous chemistry studies. In some cases, it would also be possible to contribute to the scientific objectives of a field program. Such aircraft missions should be looked on as an early opportunity to prove instrument capability. This workshop has identified two aircraft programs in which payload space may be available in the next year or two.

1. Stratosphere/Troposphere Exchange Experiment. Funded under the GTE program, both the NASA Electra and Convair 990 aircraft will be flown in the vicinity of a tropopause fold. The first flight is planned for 1984.

2. Stratospheric Aerosol and Gas Experiment (SAGE) II Satellite System Ground-Truth Program. SAGE-II is scheduled to be launched aboard the Earth Radiation Budget Satellite (ERBS) satellite in the summer of 1984. Ground-truth underflights are planned soon afterwards. The missions could deploy the NASA Electra and the Convair 990 aircraft to the middle-to-upper troposphere and lower stratosphere.

These and other opportunities should be considered in accordance with the specific technological needs of the individual experimenters who are developing heterogeneous chemistry instrument packages.

Additional Possible Field Programs

Some additional opportunities for study which would lead to useful insights into heterogeneous tropospheric chemistry include

1. Arctic Haze: Physical and chemical properties; soot-mediated chemical effects; and studies of usefulness of trace metals as source indicators

2. Acid Fog or Haze: Fog water chemistry production of acidity in clean air; and aerosol cycling through and removal in fog

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3. Urban Plume Dispersion: Chemical/aerosol tracer for dispersion of urban plumes into synoptic and global-scale dynamical systems; and materials inventories

4. Dust Storms: Long-range transport of aeolian dust above the boundary layer; and scavenging rates in clouds and precipitation

5. Primary Emissions Inventory: Quantify the potential direct emissions to the atmosphere of H_2O_2 and other compounds important to heterogeneous chemistry

6. Marine/Continental Margins: Follow the chemical evolution of clean marine air as it impinges on land; and study the ammoniation of aerosols and clouds

7. Acid Rain Experiment: Study acid precipitation in remote areas

8. Measurement of dry deposition rates of gases and aerosols on different surfaces

9. Design of a case study to determine the origin of H_2O_2 in cloud and rain water

LABORATORY STUDIES

As noted earlier, it is conceptually useful to treat aqueous reactions of atmospheric gases as a sequence of mass transfer, equilibrium, and kinetic processes. The present status of understanding of these processes is reviewed in a general way here from the perspective of setting out needs for laboratory research.

Mass Transport

Gas-phase and aqueous-phase mass transports to (or in) cloud droplets or liquid-aerosol particles are dominated by molecular diffusion and can be considered adequately well described by the present state of knowledge. Gas-phase mass transport to water drops with appreciable fall velocity is also rather well described by analytical, numerical, and ultimately (with increasing fall velocity) empirical treatments. Aqueous-phase mass transport is not on so firm a footing, but should nonetheless not be considered a high-priority research need.

Description of interfacial mass transport requires knowledge of the so-called mass accommodation coefficient α, the fraction of gas kinetic collisions on a pure water surface resulting in dissolution of the soluble gas. This quantity is not well known for solute gases generally, but is thought to range from perhaps 10^{-5} to 1 for clean solvent surfaces. The coefficient α may depend also on water activity as influenced by the concentration of other solutes in solution; for some gases important in tropospheric chemistry, even less is known about such dependence. For cloud size droplets, mass transport kinetics are insensitive to $\alpha \gtrsim 10^{-2}$, but increasingly sensitive to $\alpha \lesssim 10^{-2}$. A few recent studies have suggested α values $\gtrsim 0.01$ (Larson and Taylor, 1983; McMurry et al., 1983; and Wagner, 1982). If values of this magnitude are generally found for atmospheric gases of interest, then determination of α can take a lower priority. In the meantime, laboratory determination of mass accommodation coefficients must take a very high priority.

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The foregoing discussion pertains to uptake of gases on "clean" solvent surfaces. There is information from a number of studies that suggests that interfacial mass transport may be considerably inhibited by surfactant films, e.g., organic films on water droplets. Little is known about the prevalence of such organic films on cloud droplets in the troposphere. It would seem advisable to conduct some field measurements of a scoping nature (albeit very carefully, to avoid contamination) to examine for the presence of such films in natural clouds.

Equilibrium Thermodynamics

The equilibrium solubility of gases in water (or aqueous solution) is described by Henry's law, i.e., the aqueous-phase concentration [X] in equilibrium with a gas-phase partial pressure p_X is proportional to that partial pressure,

$$[X] = H_X p_X$$

the proportionally coefficient H_X being known as the Henry's law coefficient. For nonreactive solute gases, H_X may be measured directly by straightforward methods. In the case of gases that undergo rapid acid-base equilibria, the Henry's law concept is readily extended to encompass the conjugate species in terms of a pH-dependent effective Henry's law coefficient that may often be deduced either from studies that compare mass transport with chemical reaction rates or by means of thermochemical cycles. Henry's law coefficients are generally dependent on water activity as influenced by solute concentration. Such dependence may amount to an order of magnitude at solute concentrations in the several molar range, typically decreasing with decreasing water activity. Henry's law coefficients also exhibit temperature dependence, typically decreasing with increasing temperature.

In order to take full advantage of the quantitative aspects of trace species determination using plasma chromatography (see Technological Development section), thermodynamic data on large cluster ions are required for the relevant species. The most abundant terminal tropospheric negative ion is believed to be NO_3^-, although this remains to be proven. Laboratory data are needed to define the thermodynamic parameters which yield the rates of attachment and displacement of the important trace species to NO_3^-, leading to mixed clusters of HNO_3, HNO_2, and water. The NO_3^- ion interactions with sulfuric acid produce HSO_4^- core ion species. The clustering rates of these sulfate core ions with nitrate species, as well as SO_3, H_2SO_4, HSO_3, and water vapor, are also required.

The development of instruments which utilize mass spectroscopic methods to detect aerosol precursor gases such as NH_3, SO_3, and H_2SO_4 through their ion clusters and reaction products will require laboratory development and validation.

Kinetics

Aqueous-phase reaction kinetics and mechanisms are also to be determined by laboratory investigation. It is recommended that such studies be pursued to the point of description in terms of elementary reactions; only then can laboratory results be extrapolated with confidence to atmospheric situations of interest. Again, kinetic constants may exhibit dependence on water activity; such dependence may lead to

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acceleration or retardation of reaction rates with increasing concentration of ionic solutes, depending on reaction mechanism. The temperature dependence must also be treated.

The rates of aqueous-phase atmospheric reactions can probably be adequately described given the preceding information, and this approach to the description of such rates appears to be the appropriate course. Experiments should be designed and conducted to determine the pertinent elementary kinetic and equilibrium quantities in the most direct and least unambiguous way. It is probably not inherently necessary to carry out studies of reaction kinetics in laboratory realizations of clouds that simulate dispersion properties characteristic of natural clouds. On the other hand, there may be phenomena that are most directly studied with single particles or with aerosols or model clouds.

Finally, analogous to the ongoing program that reviews gas-phase kinetic data, a similar review effort should be initiated which is directed to kinetics and equilibria pertinent to aqueous-atmospheric chemistry. This review activity would include periodic reports tabulating rate constants, Henry's law coefficients, temperature dependence, other dependence (ionic-strength or water activity), and estimates of uncertainties in these various quantities.

Specific Study Areas

Areas of laboratory studies that are considered necessary to allow description of gas-aqueous chemistry pertinent to this program are discussed subsequently.

1. Determination of mass accommodation coefficients. As discussed previously, there is a paucity of firm data on the mass accommodation coefficient α of solute gases on water or aqueous solutions. (Parenthetically, this property is not easily measured.) Knowledge of this property is crucial to evaluations of gas-aqueous reactions in the atmosphere. However, if it can be confidently established that α values are $\geq 10^{-2}$, then gas-aqueous mass transport rates are relatively insensitive to values of α. High priority should even be given to any study that can confidently obtain α values to an order of magnitude. Infrared techniques such as Fourier transform infrared (FTIR) spectroscopy or tunable-diode laser absorption spectrometry afford the best opportunity for such laboratory measurements. Systems of highest interest are SO_2, H_2O_2, NO_3, N_2O_5, and HO_2 on clean liquid-water surfaces. These studies should then be extended to dilute and concentrated aqueous-salt solutions and to surfaces covered by an organic film. Temperature dependence would also be useful if determinations can be sufficiently refined to determine such dependence.

2. NO_x-aqueous reactions. Field studies showing formation of HONO at night suggest that this reaction may occur by heterogeneous reactions, possibly involving NO_2. Laboratory studies should investigate this. Additionally, the possibility of direct reaction of NO_3 with liquid water should be examined. Reaction of N_2O_5 with water is assumed to be rapid. This should be confirmed by laboratory study. Accommodation coefficients should be determined at least approximately as outlined previously.

3. HO_x chemistry. Uptake of HO_2 to form H_2O_2 is deemed an important in-cloud process. Again, mass accommodation coefficients are not known and should be

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determined. The Henry's law coefficient of HO_2 is known only from thermochemical evaluation and should be determined directly. The Henry's law coefficient of OH is presumed to be large, but is not known and should be determined. The chemistry of reactions leading to H_2O_2 formation in ambient air which is in contact with liquid water (Heikes et al., 1982; Zika et al., 1982) should be elucidated insofar as such chemistry may occur in addition to that which occurs in cloud water.

4. Photoassisted H_2O_2 formation. The kinetics and mechanism of the photoassisted oxidation of organics on metal oxide and/or carbon surfaces with the concomitant production of H_2O_2 should be examined, in particular the in situ photoassisted production of H_2O_2 as an intermediate reduction product of O_2 on clay surfaces with S(IV) or N(III) as substrates, e.g., Fe_2O_3 as a photoactivated, semiconducting catalyst.

5. Comparison of bulk and dispersed-phase reaction kinetics. As is argued previously, there is strong theoretical reason to believe that values of dispersed-phase (i.e., in-cloud) reactions can be evaluated from kinetic data obtained in bulk phase studies, provided appropriate account is taken of mass transport in the two types of studies. However, no experimental confirmation of this assumption is available. An unambiguous test of this assumption should be made, using a cloud reactor or single-particle levitation trap. Execution of droplet microphysics/chemistry studies under zero-gravity conditions aboard the Space Shuttle may be possible.

6. Ice-phase and frozen-solution reactions. The bulk of atmospheric liquid water is present as cloud droplets, and a significant fraction of the cloud droplets pass through an ice phase. It is possible that trace species present in the drops form pockets of high ionic-strength solutions within the ice structure when the drops freeze. The potential thus exists for substantially different chemical processes in ice particles than obtained in purely liquid hydrometeors. While some laboratory observations of this process have been made, a quantitative evaluation of its significance in the atmosphere has not. Such studies should be extended to permit such an evaluation to be conducted. Additionally, the role of ice in stabilizing species, e.g., S(IV), against reaction should be explored.

7. Aqueous-phase oxidation of aldehydes. Oxidants include O_2, O_3, and H_2O_2. The reaction may proceed directly by metal ion catalysts and/or by photoassisted pathways. Examples are

$$2RCHO + O_2 \xrightarrow[M^{n+}]{h\nu} 2RCOOH$$

$$RCHO + O_3 \rightarrow RCOOH + O_2$$

$$RCHO + H_2O_2 \xrightarrow{Fe(II)} RCOOH + OH^- + Fe(III)$$

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8. Sulfur(IV) oxidation. Despite many years of laboratory study, there remain major unanswered questions regarding mechanisms and kinetics of oxidation of sulfur(IV) pertinent to the ambient atmosphere. These processes require further investigation.

   - Oxidation by alkylhydroperoxides. Alkylhydroperoxides (ROOH) are present at measurable levels in urban and nonurban environments. Reactions of the following type are potentially important:

$$ROOH + HSO_3^- \rightarrow HSO_4^- + ROH$$

$$(R = CH_3,\ C_2H_5,\ C_3H_8)$$

     The rates of such reactions have not been studied previously.

   - Complexation of S(IV) by aldehydes. Aldehydes complex S(IV) by formation of the corresponding hydroxyalkyl sulfonic acid,

$$HSO_3^- + RCHO = RCH(OH)SO_3^-$$

     The hydroxyalkyl sulfonic acids may serve as reservoirs for S(IV) in the droplet phase, thereby affecting the partitioning of both aldehydes and S(IV) between the two phases. Additionally, the complex is much more stable against oxidation than the uncomplexed S(IV). Equilibria and kinetics in this system need further investigation.

   - Transition metal and carbon catalyzed oxidation. The details of the Fe, Mn, Cu, and C catalyzed pathways have not been fully elucidated. The effect of light should also be examined. Examination should be made for indication of free-radical reaction, e.g., by electron spin resonance (ESR) spin trapping or formation of dithionate.

   - Effects of ionic strength on important equilibria and kinetics. As emphasized previously, a major uncertainty precluding firm evaluation of global rates of heterogeneous processes is the lack of knowledge on the influence of ionic strength on these reaction rates in the concentration regimes pertinent to clear-air, liquid-water-containing aerosols (relative humidity $\geq$50 percent). To fill this need, studies must be conducted of important solubilities (e.g., H_2O_2, S(IV), and O_3) and kinetic rate coefficients in solutions of pertinent ionic strength.

Study of Reactions on Surfaces/Aqueous Phase of Aerosol Particles

At the present time there is considerable speculation in the literature concerning the importance of heterogeneous chemical reactions at the Earth's surface and in the troposphere, as well as in the stratosphere. Tropospheric aerosols provide a large available surface area and can potentially make an important contribution to

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tropospheric chemistry if reactions take place on their surface or within the aqueous-phase surrounding particles. Keesee and Castleman (1982) (see also Castleman and Keesee, 1981) and Cadle et al. (1975), among others, have speculated on the importance of surface reactions compared to homogeneous ones in the upper troposphere and lower stratosphere, showing in a few cases that the heterogeneous reactions may be of dominant importance if reaction probabilities are suitably high. Baldwin and Golden (1979) have measured reaction probabilities for a number of atmospherically important molecules and free radicals interacting with sulfuric acid surfaces. Rather appreciable interaction coefficients have been deduced for ammonia, water, H_2O_2, OH, HNO_3, N_2O_5, HO_2NO_2, and $HONO_2$, suggesting that these among others may be influenced by aerosol reactions in the troposphere where particle concentrations are much larger and hence interaction times considerably smaller than in the upper atmosphere.

Unfortunately, the area of heterogeneous chemistry includes processes not nearly as well understood as those resulting from homogeneous reactions, and work in this area is urgently needed. Many of the attempts to unravel the importance of heterogeneous processes have come through a comparison of atmospheric observations with models which account only for homogeneous chemistry, and the heterogeneous component is simply derived by difference. In other cases, investigators (e.g., Clarke and Williams 1983, Kunen et al., 1983, and Beilke and Gravenhorst, 1978) have carried out bulk aqueous-phase chemistry studies in an attempt to investigate the possible reactions which may play a role in the aqueous-phase surrounding aerosol particles. Generally, however, these have been conducted under very poorly controlled reaction conditions or under conditions not directly transferable to tropospheric applications. It is also questionable whether the bulk reactions are applicable in explaining the chemistry of small particles. A rather interesting related finding has been derived from work by researchers (Bollinger et al., 1983) at the NOAA laboratories in Boulder, CO. These researchers have found that even a metal surface such as gold, which has long been believed by surface chemists to be catalytically inactive, actually catalyzes reactions between NO_2 and CO. This finding further supports speculations that heterogeneous reactions, as yet unidentified, may play an important role in the chemistry of the troposphere.

There is an especially great need for understanding reactions on both silicate materials and on droplets of low pH representative of the fairly large sulfuric acid component that is present for many aerosols. There are many techniques now becoming available for investigating the details of surface and droplet reactions pertinent to tropospheric chemistry. These include the methods of gas interaction with droplets such as that of McMurry et al. (1983) as well as the bulk surface reactions carried out by Baldwin and Golden (1979) and Martin et al. (1980) on sulfuric acid surfaces. In the context of unraveling basic reactions, cluster techniques are also offering the promise of elucidating the individual reaction mechanisms and especially determining the role of metal ions in catalyzing certain reactions in solution. This area has been exploited by Uppal and Staley (1982); Kappes and Staley (1982); Jones and Staley (1982); Rowe et al. (1982); and Holland and Castleman (1982). In particular, such metal ions as Fe^+ and Ag^+ have been shown to catalyze reactions among gas-phase species, and it has been shown that reactions between NO_x and O_3 can be catalyzed by Na^+. In this context, cluster chemistry has great promise in unraveling the fundamental aspects of heterogeneous processes germane to the chemistry of small particles.

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Gas-to-Particle Conversion

A general system of interest in tropospheric chemistry is the system $NH_3/NO_3^-/Cl^-/SO_4^{-2}/H^+/metal^+/H_2O$ where the equilibrium vapor pressures of NH_3, HNO_3, H_2O, and HCl would be desirable to know as a function of temperature and composition. In addition, a study of the dependence of Henry's law constants on the composition of these solutions is needed for atmospherically important species such as SO_2, H_2O_2, and NO_x, etc. If measurements of the composition of the condensed phase of the aerosol and the partial pressures of the volatile species can be made, then derivations of the partial pressures from the expected vapor pressures indicate the direction of flux between the condensed and gaseous phases for each species. Also, vapor pressure data for the mixtures are necessary if models which must consider nucleation and condensation are to account properly for the transfer of species between the two phases.

Existing vapor pressure data for the $HNO_3/H_2SO_4/H_2O$ system are sparse and apparently inconsistent (see Keesee and Castleman, 1982). Some limited information on subsystems such as $NH_3/NO_3^-/SO_4^{-2}/H^+/H_2O$ and $NH_3/Cl^-/SO_4^{-2}/H^+/K^+/Na^+/H_2O$ is now being obtained by Tang et al. (1978) and Tang (1980). Henry's law constants for dilute-aqueous solutions of many atmospheric species of interest are known; however, these values are not applicable where high concentrations of solutes are present as is probably the case for the aqueous phase of tropospheric hazes or aerosols. At present, the understanding of salt effects on solubility and vapor pressures in mixed solutions is poor (Wurter, 1976), and better understanding will be required to accurately assess the partitioning of volatile species between the condensed and gaseous phase in aerosols.

Prenucleation Embryos

Spectroscopy of Small Molecules

A largely unexplored area relevant to atmospheric chemistry is the spectroscopy of small molecules that serve as prenucleation embryos. Measurement of photodissociation cross sections for such species as $SO_3 \cdot H_2O$ and coclusters with other molecules such as ammonia would be especially important to assess their likelihood of existence in the free atmosphere and would help provide the spectra needed for their qualification by spectroscopic methods. Additionally, the photochemistry of such molecules as terpenes and clusters involving their products with other atmospheric molecules would be especially important. Interactions such as those between sulfuric acid and sodium chloride-containing aerosols, leading to the formation of HCl, are not well known.

The spectroscopy of such species as NH_4NO_3 also warrants investigation. Similarly, other species formed by the interaction of acid molecules with ammonia may also lead to particle formation, and their nucleation and photo-stability require study.

Study of Multiphoton Ionization of Prenucleation Clusters

As an extension of the work on both optical spectroscopy and mass spectrometry, work should be carried out to investigate the application of multiphoton ionization techniques to small molecular clusters and related species using both nonresonant and resonance-enhanced multiphoton ionization. Effort would focus on the development of

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instrumentation and techniques suitable for studying the atmospheric concentration, size distribution, and speciation of small nucleation-mode aerosols, as well as the prenucleation embryos.

Advantage may be taken of the spectroscopic phase of the work discussed in the preceding section for performing resonance-enhanced ionization. The laboratory phase of the work should consider cluster fragmentation effects, which could adversely influence interpretation of the field measurements unless properly accounted for in the implementation of the technique.

Studies of Nucleation and Growth

At the present time, there is a paucity of basic understanding of the mechanisms leading to gas-to-particle conversion in the atmosphere. Work in this area is germane to the entire gamut of atmospheric problems including the transfer of molecules from the gaseous to the condensed phase, thereby removing them from participation in gas-phase homogeneous reactions, the influence on their lifetimes, transport, and removal processes, and introduction to potentially catalytically active surface sites. The formation of aerosol particles not only increases surface area available for reactions but also has an influence on the radiation balance of the atmosphere and on other aspects of climate such as subsequent growth and precipitation processes.

Models have been developed that account for both nucleation onto preexisting embryos and cluster-cluster interactions leading to particle formation. The advent of new experimental techniques such as molecular beams, enabling the continuous course of change in the growth and properties of small clusters to be examined, now makes this area of research amenable to scientific investigation at the molecular level on systems of direct interest in the atmosphere. An especially useful and important problem is ascertaining the sizes which small clusters must attain before they begin to display properties normally associated with the bulk condensed phase. New laser techniques and electrostatic focusing methods are providing insight into the region between the gaseous and the condensed phase and will ultimately answer the question of when particles are large enough to be adequately treated by the conventional Kelvin corrections to the vapor pressures due simply to a macroscopic effect from the surface of curvature.

There are two generally accepted mechanisms by which new aerosols can be formed in the atmosphere via gas-to-particle conversion. One is a direct nucleation mechanism by which a gas-phase molecule undergoes a phase transformation involving a heteromolecular process (bonding to an atmospheric ion or to a dissimilar molecule such as an acid or salt). The second is envisaged to occur by interaction between various preexisting quasi-stable clusters of the aerosol-forming species. The same factors governing the stability of these various complexes also contribute to a lowering of the energy barrier to direct heteromolecular nucleation, and, therefore, research on one topic contributes directly to an understanding of the other aspect of particle formation.

The cluster-cluster mechanism accounts for particle formation via ionic species of unlike sign in the atmosphere. This idea has been extended to include the growth of multiple-ion clusters in a particle and has important implications to processes which may operate in both the middle atmosphere and the troposphere.

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The results of recent work on the bonding of atmospheric molecules to ions have been used to assess those species which may be important in this context. An intriguing system comprises clusters of the important terminal negative ion NO_3^- and the analogous positive ion H_3O^+. Experiments on the hydration of HNO_3 provide evidence for the formation of an overall neutral cluster, involving separated ion pairs of these species. Related studies for other cluster ions are needed, including work on: (1) mixed clusters of acid molecules such as HNO_3 and HCl clustered with water to negative ions such as NO_3^-, (2) the foregoing neutrals together with H_2SO_4 clustered to HSO_4^-, and (3) HNO_3, HCl, H_2O, and NH_3 coclustered to H_3O^+ or NH_4^+.

Nucleation in chemically reacting vapors of neutral species at trace concentrations representative of those of tropospherically important species should also be undertaken. In this regard, the most important system for study is H_2SO_4-SO_3-H_2O. Attention to the problem of cluster-cluster interaction is required.

Additional Work

In addition to the major laboratory and field programs detailed previously, there are a number of small, independent, and important programs that could be begun immediately. Several are listed here.

In addition to the research needs, two immediate information needs were identified that can be met on a relatively short time scale and with relatively low expenditures. These needs are discussed in the Scoping Study section.

1. Scoping Study. A preliminary evaluation of global annual fluxes through atmospheric aqueous-phase processes can be made by using information presently available. Inputs to this process would be estimates of pertinent concentrations from measurements or models; where only a range can be given, the evaluation should be carried out for the extremes of this range. Additionally, the global extent of the aqueous phase within the atmosphere has to be better known. Likewise, the available surface area of the aerosol has to be better estimated on a global scale. The first information need involves the following parameters: the volume of the atmosphere that is taken up by clouds, the average liquid-water content (LWC), and the cloud droplet size distribution as a function of region and altitude, as well as of the time of day and season. Also required is some knowledge of the microphysics of the cloud, such as liquid-to-ice-phase size distributions, and of the illumination within the cloud. The second information need is increased knowledge of aerosol size distribution, concentrations, and residence times, all as functions of geographical and temporal parameters. The information from these admittedly primitive calculations will serve as input to identify key processes for more detailed study or alternatively to rule out processes as unimportant.

2. Evaluation of Aqueous-Phase Kinetic Data. There is a widespread literature of kinetic and solubility data pertinent to atmospheric aqueous-phase chemistry. However, there has been no systematic evaluative review of the data analogous to the ongoing review of gas-phase kinetic data. It is recommended that such a review be initiated, with the objective of publishing periodic evaluations of these data.

3. Exploration of Minor Sulfur Species. It seems worthwhile to devote a small amount of resources to a definitive evaluation of the importance of these

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compounds, such as elemental sulfur and the thionic species. One or two small, highly competent groups of analytical chemists should collect appropriate samples and screen them for these "nonclassical" sulfur species and, where any are found, measure their concentrations. This is primarily a laboratory exercise, initially unconnected to other recommended experiments. If significant findings result, however, this could lead to recommendations to modify ongoing field studies and/or to initiate mechanistic laboratory experiments aimed at understanding the mode of formation and/or removal of the species. Though low budget, this has high priority and can be started quickly; the sooner it is carried out, the sooner it can be learned whether present studies need modification to account for the entire sulfur budget.

MODELING

Overview

To analyze and interpret data collected in heterogeneous chemistry field experiments, models of differing scope and complexity will be required. Modeling is a key link relating data derived from laboratory studies and field measurements leading to the description of rates or processes of concern in the ambient atmosphere. For the purposes of describing atmospheric aqueous-phase reactions, it is felt that a rather modest program of modeling should suffice. Models should be directed to the examination of specific processes, and it is anticipated that a variety of models will need to be developed focusing on different processes and not all incorporating the same features. Among the models that will be useful are

1. Mass budget box model
2. Cloud droplet aqueous-chemistry model
3. One-dimensional gas/aerosol/cloud chemistry model
3. Cumulus cloud microphysics/chemistry model
3. Two- or three-dimensional transport/chemistry model

The models are listed roughly in the order of increasing complexity. Importantly, forms of all of these models currently exist, although most would require some modification to apply to specific experimental situations or to incorporate newly defined chemical and physical mechanisms.

1. Mass budget box model. In many atmospheric experiments, a physical domain can be isolated, and gross fluxes of materials into and out of that domain can be determined. Inside the domain, transformation rates can be estimated. Thus, a simple mass balance, or budget, model can be established to check the overall consistency of a set of measurements. A simple budget model also establishes the basic fluxes which determine the relative importance of competing chemical and physical mechanisms.

2. Cloud droplet aqueous-chemistry model. In view of the major role of cloud droplet models in the work proposed, various forms of such models are discussed in detail in the following sections.

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3. One-dimensional gas/aerosol/cloud chemistry model. One-dimensional (1-D) cloud chemistry models can be used to analyze large homogeneous air masses (e.g., the marine boundary layer). The 1-D model can treat chemical processes and many microphysical processes in detail, while still accounting for vertical mixing.

4. Cumulus cloud microphysics/chemistry model. Cumulus cloud microphysics/chemistry models are mechanistic models of individual clouds. The degree of parameterization of processes such as entrainment, cloud water-to-rainwater conversion processes, and air parcel kinematics depends on the dimensionality of the model. Gas-phase chemistry modules for interstitial air and the air outside the cloud can be added to existing dynamical models. The microphysical processes can be accounted for mechanistically as can the aqueous-phase chemistry processes that are coupled to them. Generally, these models resolve the drop-size spectrum, include collision and coalescent processes for droplet growth, and calculate liquid-water content.

5. Two- and three-dimensional transport/chemistry model. Multidimensional mesoscale transport models can be used to analyze the meteorology encountered in aircraft sampling. Ideally, the model would include an accurate representation of the boundary layer physics and some chemistry and aerosol physics. Such models appropriate for heterogeneous chemistry analysis are presently under development.

Modeling efforts would be most profitably directed to diagnostic or interpretive evaluations, typically in a zero- or a one-spatial dimension. Frequently, it may be entirely adequate to impose the time evolution of pertinent physical parameters (e.g., temperature, drop-size distribution, and liquid-water content) externally because it is not necessary for them to be coupled fully to gas-phase models, and to follow the response of the chemistry to this externally imposed history. Such models should, however, attempt to reproduce the salient features of cloud microphysics responsible for coupling the gas-phase and aqueous-phase chemical systems.

One-Dimensional Adiabatic Lagrangian Cloud Model

An example of a model meeting the foregoing criteria would be a one-dimensional adiabatic Lagrangian cumulus cloud model coupled to aqueous-phase chemistry of selected species of interest. This model would allow examination of the interaction of the chemical species with a varying liquid-water content which, furthermore, has a surface-to-volume ratio which will vary over several orders of magnitude over the cloud lifetime. Clearly, this will be important for absorption processes. Also, it will be possible to evaluate the effects of variable concentrations on chemical reactions. For example, is a different chemistry important at the high ionic strength typical of evaporating droplets as opposed to dilute solution during the "middle" period of the cloud life?

Examples of features to be incorporated into models are listed here. Not all features would be incorporated in all models.

1. Gas- and aqueous-phase mass transport

2. Gas-aqueous and aqueous-phase equilibria

3. Gas- and aqueous-phase reaction kinetics

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4. Chemistry in concentrated solutions characteristic of clear-air aqueous aerosol

5. Cloud microphysics, specifically including droplet growth/evaporation cycles

6. Scavenging of preexisting aerosol particles

7. Ice-phase nucleation and gas-phase ice-phase interaction

These objectives of modeling have been identified.

1. Determine nucleation scavenging efficiency of preexisting aerosols.

2. Examine the influence of the process aerosol (and gas) → haze aerosol → cloud → haze aerosol → aerosol (and gas) on the composition of the final material, for example, the extent of occurrence of the reaction H_2SO_4(AP) + NaCl(AP) → $NaHSO_4$(AP) + HCl(g). Examine effects of ionic strength corrections.

3. Examine the sensitivity of SO_2 aqueous-phase oxidation rates to assumed chemical mechanisms and input oxidant and catalyst concentrations. The catalysts are transition metals and particulate carbon.

4. Examine the sensitivity of aldehyde aqueous-phase oxidation rates to assumed chemical mechanisms and input oxidant and catalyst concentrations.

5. Examine effects of freeze-thaw processes on aqueous-phase chemistry.

Cloud Microphysics

Cloud microphysical considerations play a major role in governing the overall extent of transformation due to in-cloud processes. We note first that microphysics will determine the volume and time scale for reaction to occur. The number of cycles which a chemical species makes through cloud hydrometeors is obviously of great importance in determining the importance of clouds with regard to transformation and removal of these species. This number will be determined by the precipitation efficiency which, in turn, is determined by the precipitation mechanism, i.e., the microphysics. For example, it is well known that the precipitation efficiency of cumuliform clouds is generally lower than that of stratiform clouds. However, estimates of a global average efficiency which are now extant are clearly incorrect. Considerable work needs to be done in this area. However, from the standpoint of a chemical measurements program, interpretation of any results must involve estimates of the precipitation efficiency for the clouds examined (and hence their microphysics).

Nuclei Scavenging

Nuclei scavenging is of at least comparable importance to gas scavenging in determining the composition of clouds and should be treated at a comparable level of detail. The degree of incorporation of preexisting sulfate and various trace metals into cloud droplets will be dependent on the nuclei scavenging efficiency, which is highly variable and dependent on both cloud dynamics and microphysics. Nuclei scavenging efficiency will therefore greatly influence the initial composition of the cloud droplets and consequently strongly influence redox reactions in solutions. Indeed, since there is considerable evidence that the amount of sulfate

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produced in cloud hydrometeors is only a fraction of that incorporated from preexisting sulfate nuclei, nucleation sampling may be said to influence strongly the fractional increase in sulfates produced in a cloud.

Another aspect of the nuclei scavenging question is the possibility of nonlinear scavenging of preexisting sulfate particles. There is evidence that the scavenging efficiency for sulfate is inversely proportional to the sulfate concentration. Often, the sulfate concentration reaches some threshold. Theoretical studies suggest that this threshold is rather high (~20 $\mu g/m^3$). However, laboratory studies (cloud chamber studies) are badly needed to confirm or refute this point.

Ionic-Strength Effects

Because of the high concentrations of ionic species in aqueous clear-air aerosol and, as well, in evaporating cloud droplets, ionic-strength corrections to dilute solution (ideal) equilibria will be substantial. An immediately apparent effect of this is on the vapor pressure of volatile gaseous acids (HCl and HNO_3) that may be evolved into the gas phase on drop evaporation.

Ice Phase

The presence of significant amounts of water in the solid phase is expected to affect molecule and radical accretion, and chemical processing time scales, etc. No chemical model now includes ice effects.

TECHNOLOGICAL DEVELOPMENT

Introduction

The minimum detection limits (MDL) and sampling times required for the species to be measured in the proposed experiments are given in tables I through XXI along with the current status of available instrumentation to these measurements.

A listing of important technology issues includes

1. Development of high-volume sulfur gas and aerosol samplers for aircraft so that the detection of compounds such as SO_2, CS_2, DMS, SO_4^{2-}, and other trace species can be accomplished with cycling times of 1 to 5 minutes or less

2. Alternatively, development of new, more sensitive fast-response detection schemes for these trace species, for example, using

   - laser fluorescence or multiphoton excitation
   - active ionization -- mass spectrometry

3. Development of similar instrument techniques for other chemical cycles:

   - HO_x -- H_2O_2 (vapor and aqueous)
   - N -- HNO_3, NO_3, N_2O_5, HO_2NO_2, NH_3, NH_4^+

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- o C -- a broad range of gaseous and aqueous hydrocarbons, organic films, and elemental carbon

- o Halogens -- chlorine, iodine, and bromine compounds, as gases, solids, and in aqueous solutions

4. Development of speciation analysis as a function of aerosol particle size, where very small samples would be available. Analysis could initially focus on sulfur. Identification of metals, radionuclides, and isotopes which act as tracers of particle history should also be sought

5. Pursuit of promising devices to study heterogeneous atmospheric chemistry:

   - o heated-inlet aerosol sampling systems

   - o ion mass spectrometry

   - o laser sensors

6. Development of simpler methods to estimate accurately the rates of "dry" deposition of gases and aerosols to various surfaces

Two techniques, laser-induced fluorescence (LIF) and tunable-diode laser absorption spectrometry (TDLAS), warrant further comment for several reasons. Both are applicable to a variety of species, and significant advances have been made in both techniques since the appearance of current literature.

The H_2O_2 is believed to be a major oxidant in S(IV) to S(VI) conversion. The TDLAS and the enzyme fluorimetry techniques are the only two methods sufficiently advanced for involvement in the proposed experiments. For this reason, a brief description of the status of the fluorimetry technique is also given.

Since cloud chemistry is an integral part of the proposed experiments, required specifications for cloud water collection and interstitial air sampling are also given.

Two-Photon Laser-Induced Fluorescence (LIF) Techniques

During the last 2 years, significant progress has been made in the use of two-photon LIF techniques. The major advantage of these techniques in comparison with the single-photon LIF systems is the strong rejection of background resonance fluorescence (typically 10^5 to 10^6 greater than the single-photon LIF systems). Thus, these newly developed two-photon LIF techniques are the first of a generation of signal-limited detection systems.

The various forms of the two-photon LIF techniques have now been demonstrated for the trace gases NO (in the field) and NO_2 (in the laboratory) and show considerable potential for examining other key trace gases such as NO_3, HNO_2, OH, NH_3, SO_2, and H_2O_2.

These fast-response techniques can establish real-time vertical profiles and measure trace gases in the cloud and high-aerosol concentration environment with the extreme sensitivities that are very much needed for the studies of the atmospheric

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heterogeneous processes. Furthermore, because of its 10-Hz data collection rate, it appears to have great potential for flux measurement via the eddy correlation approach.

Tunable-Diode Laser Absorption Spectrometry

Tunable-diode laser absorption spectroscopy affords a number of attractive features for in situ, real-time tropospheric measurements. It is a universal method; in principle it is applicable to most species of tropospheric interest. It provides unequivocal identification of the species without interferences from other constituents.

Considerable advances in the detection limit, response time, and proven capability in ambient air measurements of the technique have been made since NASA CP-2292 (1983). The technique has also been extended to permit simultaneous measurement of more than one species.

The methodology has two requirements for any selected species: characterization and optimization of the optical system and development of suitable calibration and sampling procedures. These have been met and demonstrated in ambient air for NO, NO_2, H_2O_2, HNO_3, HCHO, and NH_3.

The demonstrated minimum detection limits for these gases are 100 to 300 pptv, and the response times range from 1 sec for NO, NO_2, H_2O_2, and HCHO to 100 sec for HNO_3 and NH_3. Trade-offs between MDL and time resolution are possible. Both detection limit and time resolution can be further improved using presently available hardware and software capability. Advances in laser diode performance under development should provide further improvements within the next few years.

Current instruments can provide useful information for many of the experiments being proposed. In some cases (e.g., HCHO), the laser diode instrument provides the only proven technology for the gas phase at the low concentrations found. In other cases, because of its relative freedom from interferences, it can provide important comparisons with less definitive techniques at the upper end of the concentration range anticipated in the experiment.

Cloud and Precipitation Collection

There are fundamental specifications of an airborne cloud and precipitation collection system.

1. Collect cloud water separately from aerosols. This requires typically a size cut of approximately 2 micrometers diameter below which the collection efficiency approaches zero.

2. Provide cloud water collection as a function of droplet size distribution spectrum and collect cloud water separately from rain drops by size discrimination.

3. Isolate collected water immediately from contact with the interstitial air. This may require collection devices based on the forward stagnation slot technique.

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4. Provide sampling port for interstitial air from which all cloud droplets have been removed without contamination of the air. This may require application of reverse flow or dichotomous sampling principles. This air would be usable for normal aerosol and gas analytic measurements.

5. Provide heated sampling port for evaporation of suspended cloud droplets. This would allow information about total content of gas and condensed phases.

6. Provide inert inside surfaces for all ports and plumbing leading to collection and/or analytical devices.

7. Provide a minimum collection rate of 1 ml cloud water per minute per 0.1 g m^{-3} of liquid-water content.

Devices that satisfy the above criteria are not yet fully developed. However, current collectors with proven field success do approach them and will require modifications that appear to be attainable.

Availability of methods for cloud-water-dissolved substances at a given time resolution is predicated on the availability of cloud water collection devices of suitable collection rate for the aircraft employed, as well as on the volume requirements per determination and the number of species to be determined per sample. Suitable cloud water collection devices exist for low-speed aircraft ($\lesssim$150 km h^{-1}) (Mohnen, 1980), and these can be ganged as necessary to provide an arbitrary sample collection rate. At a cloud liquid-water content in excess of 0.2 cm^3 m^{-3}, a time resolution of 1 min presents no problem. For higher speed aircraft, some development work and testing are required, but no major difficulties are foreseen.

Recommendation for an Instrument Assessment Panel

An instrument assessment program, with critical evaluation by an independent panel, similar to that provided for gas-phase reaction rate data would be of great value. It would provide planners of field and laboratory experiments with a reliable source of performance capabilities of all instruments currently available. Particular attention should be given to instruments that have participated in intercomparison of ambient air environments. Such impartial assessments would be particularly valuable for commercial instruments, for which performance claims may be somewhat exaggerated. Since improvements in instrumentation are occurring at a rapid pace, the assessment would require frequent updating.

The experimental devices which are available to measure aerosol properties for heterogeneous chemistry studies are summarized in tables XIX and XX. Not all of the instruments listed are currently operational on tropospheric aircraft. Instrument-related technology issues and novel measurement schemes presently under development are discussed subsequently.

Some of the most urgent improvements in instrument capability center around concentration measurements for gaseous sulfur compounds and for aerosol composition analysis. The sampling time required for low-concentration sulfur compounds (e.g., SO_2, CS_2, DMS, and SO_4^{2-}) could be decreased from ~20 minutes to ~1 to 5 minutes. Also needed are aerosol collection devices which can be used to distinguish aerosol composition as a function of particle size (over a discrete set of size ranges). Detectors applicable to very small aerosols in the size range from 0.001 μm to

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0.05 μm radius would be extremely helpful in determining the origins and size distribution behavior of submicron marine particles.

Within the nitrogen cycle, sensitive and accurate techniques are required for HNO_3 vapor and particulate nitrate analysis. In all cases, supporting measurements of H_2O_2 (vapor and aqueous) should be a goal.

The carbon and halogen cycles must be studied in a more coordinated manner before precise requirements for future instrumentation can be defined. With respect to the halogens, existing filter techniques for aerosol sampling and their analysis are adequate for below- and above-cloud aerosol work. Cloud water and interstitial air/aerosol collection methods exist but need to be improved for more efficient and clean separation of the phases. Denuder separation and determination of HCl in the ppt range are possible for gas-phase samples and could probably be extended to the other hydrohalides. Analysis for the free halogen gases may be difficult because of extremely low concentrations.

Techniques for measurement of formaldehyde are long-path UV adsorption and tunable-diode lasers. On board an aircraft, a sampling technique with subsequent analysis by gas chromatography or high-pressure liquid chromatography (HPLC) after derivatization is more appropriate for formaldehyde and other low-molecule weight organics.

Remote-Sensing Instrumentation

Satellite

Presently, the only systems available to make measurements of aerosol extinction profiles from a satellite are Stratospheric Aerosol Measurement (SAM II) and the upcoming SAGE II instruments. The SAM II has been making one-wavelength (1-μm) aerosol extinction measurements in the Arctic and Antarctic, due to its orbital characteristics. The SAGE II instrument is scheduled to be launched aboard the Earth Radiation Budget Satellite (ERBS) during late summer of 1984. The SAGE II will measure aerosol extinction coefficients at three wavelengths at altitudes from cloud tops to about 35 km, H_2O from cloud tops to about 22 km, O_3 from cloud tops to about 55 km, and NO_2 from 18 km to 45 km.

These instruments obtain global-scale aerosol information in the form of two quite separated vertical extinction profiles measured during each revolution of the spacecraft at each spacecraft sunrise and sunset. Each subsequent sunrise or sunset, however, is separated from the previous one by 24° in longitude and <1° in latitude. The satellite field of view is along the Earth's limb, with a 0.5 km to 1.0 km vertical resolution and a 200 km to 300 km Sun/satellite limb path length. In most cases, a single SAGE II extinction profile measurement would not be useful in determining important heterogeneous phenomena, but a large number of these multi-wavelength extinction measurements distributed over latitude and longitude could be used to infer changes in the aerosol size distribution and other properties, as a function of location and time. Aerosol sources, sinks, and exchange processes could also be studied in the upper troposphere and stratosphere.

Even though the predecessor SAGE I satellite was designed only for stratospheric measurements, the 3-year SAGE I data set demonstrates that a limb measuring instrument can probe down to the midtroposphere 50 percent of the time (i.e., cloud-free limb paths occur that frequently).

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A vigorous absolute calibration, or "ground truth", program is planned for SAGE II. This program represents a large aerosol field experiment in which heterogeneous processes could be studied with the addition of a few carefully selected measurements. Either the NASA Electra or Convair 990 will be used for the SAGE II calibration measurements. Meteorological support sensors and a number of balloon-borne instruments will also participate. Water vapor, NO_2, and O_3 will be measured in addition to the aerosol size distribution, composition, and mass.

During the SAGE II ground truth program, testing, calibration, and intercomparison of instruments under development for the MBL experiment and other heterogeneous tropospheric chemistry programs could be carried out. Independent experiments might also be designed for the cold tropopause region where the aircraft would fly. For example, condensation nuclei formation might be enhanced in this region and would be detectable.

Other experiments which are possible in connection with the SAGE II program involve clouds and the region just above clouds. The SAGE II has the capability to measure H_2O down to the cloud tops, in addition to the aerosol extinction at three wavelengths. The H_2O vapor content above the cloud tops is important to understanding the stratosphere H_2O source/sink relationship for towering cumulus clouds with extensive anvils. Aerosol extinction might show a change associated with the formation of new particles (perhaps ice). The SAGE II will make such measurements around the globe providing an opportunity to study tropospheric water vapor injection into the stratosphere on a regular basis. The SAGE I data have already shown that cirrus clouds (which appear in extinction) frequently occur in the tropical stratosphere one or more kilometers above the tropopause, predominantly in a few regions such as Micronesia.

Lidars

Lidars can measure the aerosol backscatter intensity at a number of wavelengths between about 0.3 μm to 1.06 μm and near 10.6 μm. From a medium-altitude aircraft platform, these data can be used to map the aerosol spatial distribution, which reflects air motions. Vertical and horizontal resolutions are of the order of 10's of meters. Lidars can also be used in a differential absorption mode (one wavelength on and one wavelength off of an absorption feature) to measure O_3, H_2O, and possibly other gases. The O_3 and H_2O measurements are reported in the literature. Because of signal-to-noise (S/N) considerations, the vertical and horizontal resolutions are not as good as in the aerosol measurements (about 1 km in the vertical and about 2 km in the horizontal). A downlooking lidar on a high-altitude aircraft could map the tops of cirrus, cumulonimbus, and stratus, and determine the boundary layer height and structure.

Tunable-Diode Laser System (TDL)

In principle, the tunable-diode laser (TDL) system with heterodyne detection can detect atmospheric species at wavelengths between about 4 to 12 μm, with a resolution of the order of about 10^{-4} cm^{-1} throughout the infrared range. Such resolution allows the potential measurements of any gas with sharp rotational structure (lighter molecules). For example, gases as ClO, H_2O_2, HO_2NO_2, $ClONO_2$, SO_2, HOCl, and HCl, etc., could be measurable. An instrument of this type, which is under development and has already measured O_3 spectra using the Sun as a source, will not be ready for aircraft flights before 1986.

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The TDLs are already in use for in situ absorption measurements. For example, they have been used on aircraft to measure CO, and on the ground to measure NH_3, HNO_3, and formaldehyde. These systems could be used to measure the precursor and product gases associated with heterogeneous processes.

Plasma Chromatography

It has been known for some years that the technique called "plasma chromatography" is of value in assessing the presence of certain species in the gas phase which cluster to a variety of different ions. In its typical configuration, a plasma chromatograph operates at atmospheric pressure, and a radioactive source of ionization is frequently employed to produce either positive or negative ions which are transported to a detector in a carrier gas. In more recent developments, selective ionization is initiated with laser radiation. The reactant ions thus produced undergo subsequent ion-molecule reactions with trace molecules either present in, or injected into, the carrier gas stream. The resultant product ions are separated in a coupled ion-drift spectrometer to obtain positive or negative mobility spectra which bear a relationship to the molecules involved and the reactant ions generated. Other techniques involve direct measurements with mass spectrometers, but usually these can only be applied at low pressures which are typical of the upper troposphere and above. Crucial in qualitatively interpreting the data acquired from either technique is information on the extent of clustering, stability, and rates of formation of the various complexes observed. Arnold (1982) and Eisele (1983) have recently demonstrated the possibility of making meaningful measurements in the lower troposphere, suggesting the likelihood that these methods will soon be available for quantitative study of both ions and trace atmospheric species. In fact, Arnold's measurements are the first to have provided direct evidence for the species HSO_3. Previously, it had only been speculated to be the reaction product of OH with SO_2.

Enzyme Fluorimetry

Enzyme fluorimetry is a sensitive technique for real-time in situ determination of peroxides in liquid-phase and ambient air samples. Hydrogen peroxides and organic peroxides are determined by the use of a dual-beam fluorimeter with one channel determining the total peroxides and the second channel determining total peroxides minus hydrogen peroxide that has reacted with added catalase.

Progress in the last year has lowered the minimum detectable limits to <20 pptv H_2O_2 for the gas-phase instrument and <100 pptm H_2O_2 for the liquid-phase instrument. Testing the vapor-phase instrument with atmospheric levels of SO_2, NO, NO_2, O_3, and hydrocarbons gives <5 percent interference in 500 pptv H_2O_2 signals. Testing at reduced pressures (~500 mb) shows the gas-phase peroxide instrument is linear with pressure. The liquid-phase instrument, with a coefficient of variation of 0.9 percent, has been tested with more than 25 possible interferents, and none has given appreciable interference.

Enzyme fluorimetry is a well-tested technique that is very suitable to measurements at remote field sites and on aircraft missions due to its low weight requirement (~70 lb), low power consumption (~300 watts), and ability to perform at low ambient pressures. The instruments for the liquid-phase and the vapor-phase peroxides are both automated and entail minimal demand for operator attention. Since their calibrations are related to the same standard, they provide an ideal approach to the investigation of heterogeneous oxidation processes.

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Mass Spectrometer Techniques

Especially important in clarifying the nucleation of new aerosol particles is work on the existence and growth of such prenucleation embryos as sulfuric acid-water clusters, and on the incorporation of other molecules into the growth aggegates such as nitrates, chlorides, sulfates, and ammonia. A combination of mass spectrometry and mobility analyses is expected to provide the best opportunity for studying matter in the state of aggregation between small molecular clusters and the small aerosol particles, which is crucial in elucidating gas-to-particle conversion processes. Laboratory studies will be required in the initial phases of instrument development. Later, the two methods would be applied to a study of clusters in the nucleation-size mode. Use of multiphoton ionization will enable an investigation of the larger cluster regime with mass spectrometer techniques. Laboratory studies of cluster distributions using these detection techniques are required for the relevant neutral acid-water cluster species. Multiphoton experiments conducted in the laboratory have been successfully implemented to study the distribution of neutral heteromolecular cluster embryos, and offer promise that such methods can be used to determine the chemical composition of both prenucleation embryos and the small nucleation aerosol mode as a function of size.

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REFERENCES

Arnold, F.: Nature, vol. 299, p. 134, 1982.

Baldwin, A. C., and Golden, D. M.: Science, vol. 206, p. 562, 1979.

Beilke, S., and Gravenhorst, G.: Atmos. Environ., vol. 12, p. 231, 1978.

Bollinger, M. J., Sievers, R. E., Fahey, D. W., and Fehsenfeld, F. C.: Anal. Chem., vol. 55, p. 1980, 1983.

Cadle, R. D., Crutzen, P., and Ehhalt, D.: J. of Geophys. Res., vol. 80, p. 3381, 1975.

Calvert, J. G., and Stockwell, W. R.: Can. J. Chem., vol. 61, p. 983, 1983.

Carlson, T. N.: Monthly Weather Review, vol. 107, p. 322, 1979.

Carlson, T. N., and Prospero, J. M.: J. Appl. Meto., vol. 11, p. 283, 1972.

Castleman, A. W., Jr., and Keesee, R. G.: Annual Review of Earth and Planetary Sciences, vol. 9, p. 227, 1981.

Chameides, W. L., and Davis, D. D.: J. Geophys. Res., vol. 87, p. 4863, 1982.

Chameides, W. L., and Davis, D. D.: Nature, vol. 304, p. 427, 1983.

Chatfield, R. B.: Remote Tropospheric SO_2: Cloud Transport of Reactive Sulfur Emissions. Ph.D. Thesis, Colorado State Univ., 1982.

Ching, J. K. S.: Extended Abstracts of the Third Joint Conference on Applications of Air Pollution Meteorology, American Meteorological Society and the Air Pollution Control Association, San Antonio, Texas, January 1982, p. 5, 1982.

Clark, A. G., and Williams, P. T.: Atmos. Environ., vol. 17, p. 617, 1983.

Crutzen, P. J., Heidt, L. E., Krasnec, J. P., Pollack, W. H., and Seiler, W.: Nature, vol. 282, p. 253, 1979.

Daum, P. H., Schwartz, S. E., and Newman, L.: Precipitation Scavenging, Dry Deposition, and Resuspension, H. R. Pruppacher, R. G. Semonin, and W. G. N. Slinn, eds., Elsevier, N.Y., p. 31, 1983.

Daum, P. H., Schwartz, S. E., and Newman, L.: J. Geophys. Res., vol. 89, p. 1447, 1984.

Duce, R. A., Arimoto, R., Ray, B. J., Unni, C. K., and Harder, P. J.: J. Geophys. Res., vol. 88, p. 5321, 1983.

Eisele, F. L.: Direct Tropospheric Ion Sampling and Mass Identification, International J. Mass Spectrometry and Ion Processes, vol. 54, p. 119, 1983.

Emmitt, G. D.: J. Atmos. Sci., vol. 35, p. 1485, 1978.

BEST COPY AVAILABLE

Ferek, R. J., Lazrus, A. L., and Winchester, J. W.: Atmos. Environ., vol. 17, p. 1545, 1983.

Gidel, L. T.: J. Geophys. Res., vol. 88, p. 6587, 1983.

Gill, P. S., Graedel, T. E., and Weschler, C. J.: Rev. of Geophys. and Space Phys., vol. 21, p. 903, 1983.

Gillette, D. A., and Blifford, I. H.: J. Atmos. Sci., vol. 28, p. 1199, 1971.

Greenhut, G. K., Repoff, T. P., and Ching, J. K. S.: Extended Abstracts of the Third Joint Conference on Applications of Air Pollution Meteorology, San Antonio, Texas, January 1982, p. 17, 1982.

Harris, J. M.: NOAA Tech. Memo, ERL ARL-116, 1982.

Harrison, R. M., and Pio, C. A.: Atmos. Environ., vol. 17, no. 7, p. 1261, 1983.

Hegg, D. A., and Hobbs, P. J.: Atmos. Envir., vol. 15, p. 1957, 1981.

Hegg, D. A., and Hobbs, P. J.: Atmos. Envir., vol. 16, p. 2663, 1982.

Hegg, D. A., and Hobbs, P. J.: Proceedings of Fourth Intern. Conf. on Precipitation Scavenging, Dry Deposition, and Resuspension, Elsevier, NY, p. 79, 1983.

Heikes, B. G., and Thompson, A. M.: J. Geophys. Res., vol. 88, no. C15, p. 10,883, 1983.

Heikes, B. G., Lazrus, A. L., Kok, G. L., Kunen, S. M., Gandrud, B. W., Gitlin, S. N., and Sperry, P. D.: J. Geophys. Res., vol. 87, p. 3045, 1982.

Holland, P. M., and Castleman, A. W.: J. Chemical Phys., vol. 76, p. 4195, 1982.

Hong, M. S., and Carmichael, G. R.: A Compartmental Model for the Characterization of Two-Gas Dispersed Hydrometeor Interactions, Paper presented at the Second Symposium on the Composition of the Nonurban Troposphere, American Meteorological Society, American Geophysical Union, and NASA, Williamsburg, VA, May 25-28, 1982.

Jones, R. W., and Staley, R. H.: J. Phys. Chem., vol. 86, p. 1387, 1982.

Kappes, M. M., and Staley, R. H.: J. Amer. Chem. Soc., vol. 104, p. 1813, 1982.

Keesee, R. G., and Castleman, A. W., Jr.: Topics in Current Physics, vol. 28, the Stratospheric Aerosol Layer, R. C. Whitten, ed., Springer-Verlag (Berlin), p. 69, 1982.

Kessler, C.: Gasförmige Salpetrige Säure (HNO_2) in Der Velasteten Atmosphäre. (Gaseous Nitrous Acid (HNO_2) in the Polluted Atmosphere), KFA, Julich, 1984.

Kunen, S. M., Lazrus, A. L., Kok, G. L., and Heikes, B. G.: J. Geophys. Res., vol. 88, p. 3671, 1983.

Larson, T. V., and Taylor, G. S.: Atmospheric Environment, vol. 17, no. 12, p. 2489, 1983.

BEST COPY AVAILABLE

Lee, Y.-N., and Schwartz, S. E.: J. Geophys. Res., vol. 86, p. 11971, 1981.

Lee, Y.-N., Senum, G. I., and Gaffney, J. S.: Peroxyacetyl Nitrate (PAN) Stability, Solubility, and Reactivity - Implications for Tropospheric Nitrogen Cycles and Precipitation Chemistry. Fifth International Conference of the Commission on Atmospheric Chemistry and Global Pollution; Symposium on Tropospheric Chemistry, Oxford, England, Aug. 1983.

Levine, S. Z., and Schwartz, S. E.: Atmos. Environ., vol. 16, no. 7, p. 1725, 1982.

Likens, G. E., Edgerton, E. S., and Galloway, J. N.: Tellus, vol. 35B, p. 16, 1983.

Logan, J. A.: J. Geophys. Res., vol. 88, p. 10785, Dec. 1983.

Martin, L. R., Judeikis, H. S., and Wan, M.: J. Geophys. Res., vol. 85, p. 5511, 1980.

McMurry, P. H., Takano, M., and Anderson, G. R.: Environ. Sci. and Tech., vol. 17, no. 6, p. 347, 1983.

Mohnen, V. A.: Atm. Technol., vol. 12, p. 20, 1980.

National Academy of Sciences, Global Tropospheric Chemistry: A Plan for Action. Global Tropospheric Chemistry Panel, Board on Atmospheric Tropospheric Sciences and Climate, National Academy Press, Washington, DC, 1984.

National Aeronautics and Space Administration, Assessment of Techniques for Measuring Tropospheric N_xO_y, NASA CP-2292, 1983.

Otterman, J., Fraser, R. S., and Bahethi, Om P.: J. Geophys. Res., vol. 87, p. 1270, 1982.

Parrington, J. R., and Zoller, W. H.: Science, vol. 220, p. 195, 1983.

Phelan, J. M.: Volcanoes As a Source of Volatile Trace Elements in the Atmosphere, Ph.D. Thesis, Dept. of Chemistry, Univ. of Maryland, College Park, MD, 1983.

Prospero, J. M.: Geol. Soc. of Amer. Special Paper 186, p. 71, 1981.

Rahn, K. A.: Atmos. Environ., vol. 15, p. 1447, 1981.

Rahn, K. A., and Lowenthal, D. H.: Science, vol. 223, p. 132, 1984.

Rahn, K. A., Borys, R. D., and Shaw, G. E.: Geol. Soc. of Amer. Special Paper 186, p. 37, 1981.

Rahn, K. A., Lewis, N. F., and Lowenthal, D. H.: Elemental Tracers of Canadian Smelter Aerosols Transported Into Northeastern United States, Receptor Models Applied to Contemporary Pollution Problems, S. Dattner and P. K. Hoppe, eds., Air Pollution Control Association, Pittsburgh, PA, 1983.

Rowe, B. R., Viggiano, A. A., Fehsenfeld, F. C., Fahey, D. W., and Ferguson, E. E.: J. of Chem. Phys., vol. 76, p. 742, 1982.

BEST COPY AVAILABLE

Schryer, D. R., ed.: Heterogeneous Atmospheric Chemistry Geophysical Monograph 26. American Geophysical Union, Washington, DC, 1982.

Schwartz, S. E.: Mass-Transport Considerations Pertinent to Aqueous-Phase Reactions of Gases in Liquid-Water Clouds. Paper presented at the NATO Advance Study Institute on Chemistry of Multiphase Atmospheric Systems, Corfu, Greece, Sept. 26-Oct. 8, 1983.

Schwartz, S. E., and Newman, L.: Atmos. Environ., vol. 17, p. 2629, 1983.

Scott, B. S.: Atmos. Environ., vol. 16, p. 1735, 1982.

Seinfeld, J. H., Allario, F., Bandeen, W. R., Chameides, W. L., Davis, D. D., Hinkley, E. D., and Stewart, R. W.: Report of the NASA Working Group on Tropospheric Program Planning, NASA RP-1062, 1981.

Staehelin, J., and Hoigné, J.: Environmental Science and Technology, vol. 16, p. 676, October 1982.

Tang, I. N.: Atmos. Environ., vol. 14, p. 819, 1980.

Tang, I. N., Mankelwitz, H. R., and Davis, J. G.: J. Aerosol Science, vol. 9, p. 505, 1978.

Thompson, A. M., and Cicerone, R. J.: J. Geophys. Res., vol. 87, p. 8811, 1982.

Uppal, J. S., and Staley, R. H.: J. of Amer. Chem. Society, vol. 104, p. 1238, 1982.

Wagner, P. E.: Aerosol Growth by Condensation, Topics in Current Physics-29, Aerosol Microphysics II, W. H. Marlow, ed., Springer-Verlag (Berlin), p. 129, 1982.

Wurter, W. F., ed.: Thermodynanic Behavior of Electrolytes in Mixed Solvents, Advance in Chemistry Series, no. 155, Amer. Chem. Society, Washington, DC, 1976.

Zika, R. G., Saltzman, E., Chameides, W. L., and Davis, D.: J. Geophys. Res., vol. 87, p. 5015, 1982.

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TABLE I.-ANALYTICAL CAPABILITIES FOR CH_4, C_2H_6, C_2H_4, and C_3H_8

(Gases)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Precision[3]	Interferences/ Constraints
Flame Ionization Gas Chromatography	4	3	1 ppb	10 min	0.2%	None identified

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

TABLE II.-ANALYTICAL CAPABILITIES FOR CO

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Precision[3]	Interferences/ Constraints
Catalyst Flame Ionization Gas Chromatography (GC)	3	2	4 ppb	10 min	0.4%	None identified
Mercuric Oxide Reduction and Atomic Absorption Detection	3	2	10 ppb	5 min	1%	H_2 and other reducing species unless separated by GC or removed by absorbents
Tunable-Diode Laser IR Absorption	3	2	1 ppb	10 sec	2%	None identified

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

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TABLE III.-ANALYTICAL CAPABILITIES FOR CO_2

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Precision[3]	Interferences/ Constraints
Nondispersive Infrared Absorption	4	1	3 ppmv	0.2 to 20 sec (limited by the physical transport of gas & calibration	0.04%	H_2O, O_2 pressure broadening
Dual-Catalyst Flame Ionization Gas Chromatography	3	3		8 min	0.04%	None identified
Precision Manometer	3	4		4 hr	0.02%	N_2O

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

TABLE IV.-ANALYTICAL CAPABILITIES FOR HNO_3

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Interferences/ Constraints
Photofragmentation Laser-Induced Fluorescence	1	1	15 ppt	1 min	TBD	10%	TBD/temperature changes, laser rep. rate
Long-Path UV Absorption	4	4	20 ppt	10 min (10 km)	20%	5%	None known/pathlength limited by visibility
Condensation	4	3	15 ppt	1 hr	TBD	5%	PAN/temperature changes, cannot distinguish hydrolysis products
Tunable-Diode Laser (TDL)	3	1	0.8 ppb				

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

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TABLE V.- ANALYTICAL CAPABILITIES FOR HNO_3

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Chemiluminescence with Converter	4	1	100 ppt	10 sec	15%	5%	0.5 ppb	None known/serious absorption problems
Tunable-Diode Laser Absorption	4	1	300 ppt	60 sec	10%	5%	6 ppb	Temperature changes, high aerosol concentration
Direct Denuder Tube (Tungstic Acid) with Chemiluminescence (CL) Detector	3	3	70 ppt	40 min	20%	10%	2 ppb	TBD/must separate NH_3
Direct Denuder (Na_2F) with CL Detector	3	3	20 ppt	8 hr	20%	10%	NA	None known
Denuder Difference, IC Analysis	4	3	100 ppt	30 min	20%	5%	0.2 ppb	Coarse particle nitrate
Filter Pack	4	3	10 ppt	60 min	20%	2%	15 ppt	NH_4NO_3, high aerosol loading
Condensation Collection	4	3	10-90 ppt	30 min	TBD	5%	NA	Hydrolysis of organic nitrates/ temperature changes
Long Path FT-IR Spectroscopy	4	1	5 ppb	5 min (1 km)	20%	5%	NA	None identified

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

TABLE VI.-ANALYTICAL CAPABILITIES FOR NH_3

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Oxalic Acid Denuder	4	3	100 ppt	4 hr	15%	15%	NA	Evap. of oxalic acid, NH_4NO_3
Citric Acid Denuder	3	3	100 ppt	4 hr	15%	5%	5 ppb	None known
Tungstic Acid Denuder, Converter and CL Detector	3	2	100 ppt	40 min	TBD	5%	5 ppb	TBD
Acid-Impregnated Filter Pack	4	3	0.2 ppb	3 hr	20%	2%	NA	Loss or gain of NH_3 on pre-filter/blank variability
Fluorescence Derivatization	4	1	0.2 ppb	3 min	20%	10%	4 ppb	Gaseous primary amines/ temperature dependence
Condensation Collection	3	3	0.15 ppb	30 min	TBD	5%	NA	Volatility of ammonium salts
Tunable-Diode Laser Absorption	4	1	0.2 ppb	1 min	30%	5%	5 ppb	None known
Long-Path FTIR[4] Spectroscopy	4	1	3 ppb (1 km)	5 min	30%	5%	10 ppb	None known
Photofragmentation Laser-Induced Fluorescence	2	1	10 ppb	1 min	TBD	TBD	NA	None known/limited by laser rep. rate
IR Heterodyne Radiometry	4	4	0.5 ppb	1 min	15%	10%	NA	Limited in detecting small volume variability

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).
[4]Fourier Transform Infrared (FTIR).

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TABLE VII.- ANALYTICAL CAPABILITIES FOR NO

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Ozone Chemiluminescence	4	1	5 ppt	1 sec	10%	5%	7 ppt	None known/detection limit dependent on water vapor concentration
Single-Photon Laser-Induced Fluorescence	3	1	30 ppt	1 min	15%	10%	70 ppt	None known
Two-Photon Laser-Induced Fluorescence	2	1	5 ppt	1 min	15%	2%	400 ppt	None known
Lidar Laser-Induced Fluorescence	3	4	5 ppt	1 sec (1 km)	15%	2%	NA	Solar flux, white fluorescent noise/ clouds, high aerosol concentration, temp. changes
Multi-Photon Ionization	1	1	1 ppb	1 sec	TBD	5%	NA	NO_2, RNO_2/temperature changes
Tunable-Diode Laser	4	1	0.1 ppb	1 sec	10%	5%	6 ppb	None known/temperature changes
Resonant Ion Laser	2	1	10 ppb	1 sec	TBD	TBD	NA	NO_2, RNO_2/temperature changes, limited UV laser energy
Long-Path UV Absorption	4	4	100 ppt	5 min (1 km)	20%	5%	NA	None known/high aerosol concentration

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

TABLE VIII.- ANALYTICAL CAPABILITIES FOR NO_2

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Ozone Chemiluminescence (NO_2 to NO Converter)	4	1	10 ppt	1 sec	30%	5%	25 ppt	PAN, other organic nitratus/detection limit dependent on water vapor concentration
Chemiluminescence (Luminol)	3	1	30 ppt	1 sec	TBD	TBD	NA	PAN, other organic nitrates/no NO interference
Gas Chromatography	2	3	3 ppb	10 min	15%	5%	NA	CO_2, other electron capture sensitive trace gases
Photofragmentation Laser-Induced Fluorescence	2	1	100 ppt	1 sec	15%	5%	4 ppt	TBD/temperature changes, laser energy and rep. rate
Multiphoton Ionization	1	1	1 ppt	1 sec	TBD	TBD	NA	RNO_2/temperature changes, UV laser energy and rep. rate
Tunable-Diode Laser	4	1	0.1 ppb	1 min	10%	5%	NA	None known/temperature changes
Resonant Ion Laser	1	1	1 ppb	NA	NA	NA	NA	RNO_2/temperature changes, UV laser energy and rep. rate
Long-Path UV Absorption	4	4	100 ppt	1 min (1 km)	20%	5%	NA	None known high aerosol concentration, high O_3; pathlength limited by visibility
Photothermal:								
Photoacoustic	2	1	5 ppb	100 sec	TBD	5%	1 ppb	H_2O, aerosols/temp. changes
Resonant Photoacoustic	2	1	2 ppb	3 min	TBD	5%	1 ppb	NO_2, O_3, aerosols
Zeeman Modulated	1	1	TBD	TBD	TBD	TBD	NA	None known

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

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TABLE IX.- ANALYTICAL CAPABILITIES FOR NO_3

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Interferences/ Constraints
Photofragmentation Laser-Induced Fluorescence	1	1	20 ppt	1 sec	TBD	10%	TBD/temperature changes, laser rep. rate
Long-Path UV Absorption	4	4	1 ppt	5 min (10 km)	30%	5%	None known/water vapor, high aerosol concentration; path length limited by visibility
Tunable-Diode Laser Absorption	1	1	100 ppt	NA	10%	5%	None known/TBD

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

TABLE X.-ANALYTICAL CAPABILITIES FOR O_3

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
UV Absorption (Commercial)	4	1	1 ppb	30 sec	10%	2%	10 ppb	None identified
UV Absorption (Special)	3	1	0.5 ppb	1 sec	NA	NA	NA	None identified
Ethylene Chemiluminescence	4	1	1-2 ppb	1 sec	10%	5%	10 ppb	None identified/ accuracy dependent on ozone source
KI Wet Chemical	4	3	1 ppb	20 sec	5%	2%	NA	NO_2, H_2O_2 and other oxidants

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

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TABLE XI.-ANALYTICAL CAPABILITIES FOR OH

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Precision[3]	Interferences/ Constraints
Radio Carbon Tracer[4]	4	4	10^5/cc	100 sec	20%	Methaloxide radical (HCH_2O)
Two-Wavelength Single-Photon Laser-Induced Fluorescence/In Situ[5]	4	3	5×10^6/cc	20 min		Laser-generated OH; aerosol fluorescence
Two-Photon Laser-Induced Fluorescence/In Situ	2	2	2.5×10^5/cc			None
Two-Wavelength Laser-Induced Fluorescence/ Lidar[5]	4	4	5×10^6/cc	20 min		Laser-generated OH; aerosol fluorescence
Low-Pressure Laser-Induced Fluorescence	2	2	10^6/cc	6 min		Wall loss of OH
308-nm Laser-Induced Fluorescence	1	2	TBD			
High-Rep Rate Laser-Induced Fluorescence	3	2	10^6/cc	20 min		Aerosol fluorescence

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).
[4]Ground-based system.
[5]Not yet routinely available.

TABLE XII.-ANALYTICAL CAPABILITIES FOR PAN

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Chemiluminescence with Converters	2	1	TBD	TBD	TBD	TBD	NA	Possibly organic nitrates. H_2O_2/selectivity of PAN converter to be established
Long-Path FT-IR Spectroscopy	4	1	1 ppb	10 sec (100 m)	25%	10%	NA	TBD
Gas Chromatography-Electron Capture Detection	4	3	5 ppt	1 min	15%	15%	40 ppb	None known/residual water vapor on column

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

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TABLE XIII.- ANALYTICAL CAPABILITIES FOR SO_2, H_2S, AND ORGANO SULFUR COMPOUNDS

(Gas)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Sulfur Dioxide:								
Pulsed Fluorescence	4	1	3 ppbv	1-2 min	±5%	3%	5 ppbv	None identified
Gas Chromatography/ Flame Photometric Detection	3	3	20 pptv	3-5 min	±5%	10%	100 pptv	Adsorption, baseline shifts from H_2O
Continuous-Flame Photometry with Particle Filter	4	1	0.3 ppbv	5 sec	10%	5%	0.4 ppbv	Selective scrubbing of RSH, H_2S required
Condensation Collection/Ion Chromatography	3	2	10-50 pptv	30 min	TBD	TBD	NA	H_2S, readily oxidizable sulfur
IIIPol Filter Pack-CO_3^{2-} Impregnated Cellulose	4	2	100 pptv	30 min	10%	5%	1 ppbv	Lowered efficiency at v. low RH
Automated West-Gaeke Colorimetry	4	3	<1 ppbv	60 min	10%	5%	1 ppbv	Possible interferents: Cl_2, HCl, H_2S, aldehydes
KI Wet Chemical w/Scrubber	3	1	3 ppbv	20 sec	20%	5%	5 ppbv	NO_2, H_2O, reductants
Liquid Chemiluminescence w/$KMnO_4$	2	3	10 pptv	15 min	20%	10%	NA	None identified
Differential Optical Absorption Spectroscopy	3	1	100 pptv	5 min (2 km)	20%	5%	NA	None identified
Tunable-Diode Laser IR Absorption	3	1	0.3 ppbv	0.1 sec	10%	5%	5 ppbv	None identified
Single-Photon Laser-Induced Fluorescence	3	1	3 pptv	1 min	15%	10%	NA	None identified
Hydrogen Sulfide:								
Impregnated Tape/ Photometry	4	2 or 3	0.2 ppbv	60 min	20%	10%	5 ppbv	Thiols interfere
Gas Chromatography/Flame Photometric Detection	4	3	20 pptv	3-5 min	15%	10%	0.2 ppbv	Severe adsorption problem
Methylene Blue Colorimetry	3	3	1 ppbv	120 min	10%	5%	5 ppbv	Protect from light, high NO interferes
Fluorescence Quenching	3	3	<0.2 ppbv	60 min	TBD	20%	1 ppbv	NO_2 interferes
Ozone-Chemiluminescence	2	1	1 ppb	2 sec	TBD	10%	5 ppbv	Organosulfur compounds
Organosulfur Compounds:								
Dimethyl Sulfide (DMS) by Chemisorption/Gas Chromatography/FPD	4	3	0.5 pptv	30 min	6%	2%	100 pptv	High levels of SO_2
COS by Cryogenic Trapping/GC/FPD	4	3	100 pptv	20 min	10%	5%	0.5 ppbv	None identified
Thiols, DMS by O_3-Chemiluminescence	2	1	100 pptv	5 sec	TBD	10%	2 ppbv	H_2S, CH_3 interference can be eliminated; high olefins interfere

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

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TABLE XIV.-ANALYTICAL CAPABILITIES FOR TRACE METAL VAPORS

Technique	Development Status[1]	Sampling Mode[2]	Detection Limit	Time Resolution	Interferences/ Constraints
Activated charcoal column	3	4	~1 ng/m^3	1 hr	Collection efficiency influenced by temperature and humidity, specific interferences are a function of analytical technique
Noble metal adsorber	3	4	<1 ng/m^3	1 hr	See above
Airborne mercury spectrometer	3	3	2-5 ng/m^3	10 min	SO_2

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.

TABLE XV.-ANALYTICAL CAPABILITIES FOR ALDEHYDES

(Gas and Aqueous)

Technique	Development Status[1]	Sampling Mode[2]	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
HCHO (gas):								
Colorimetric/ DNPH[4] derivatization & LC[5]	4	3	1 ppbv	1 hr	15%	5%	5 ppbv	Interferences separated by LC
Differential Optical Absorption Spectroscopy	2	3	0.6 ppbv	5 min (2 km)	20% TBD	5%	NA	NO_2 at high concentrations
HCHO (aqueous):								
Chemiluminescence (gallic acid, H_2O_2, pH 12.5)	4	3	100 pp	5 min	NA	NA	NA	None identified at low concentrations
Colorimetric (pararosaniline-bi-sulfite)	4	3	1 ppbm	1 hr	NA	NA	NA	None identified at low concentrations
Colorimetric (DNPH derivatization & LC)	4	3	15 ppbm	1 hr	15%	5%	75 ppbm	None identified
Colorimetric (MBTH)[6]	4	3	~10 ppbm	1 hr	15%	10%	NA	Total aldehyde measurement
Other Aldehydes:								
Colorimetric (DNPH derivatization & LC)	4	3	15 ppbm (for HCHO)	1 hr	15%	5%	75 ppbm	Acetone interferences with C_2H_5CHO det'n.

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).
[4]2,4-Dinitrophenyl Hydrazine (DNPH)
[5]Liquid Chromatography (LC)
[6]2-Methyl Benzothiazolone (MBTH)

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TABLE XVI.-ANALYTICAL CAPABILITIES FOR H_2O_2

(Gas and Aqueous)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Gas:								
Bubbler/Luminol Chemiluminescence	4	2	0.05 pgbv	15 min	Envt.-Dependent	5%	NA	Metal ions(?), oxidants/ in situ production of peroxide
Condensation Collection/ Fluorescence	3	3	TBD (v. low)	30 min	TBD	5%	NA	In situ production
Tunable-Diode Laser Absorption	3	1	1 pgbv	1 min	10%	5%	NA	None identified
Photofragmentation Laser-Induced Fluorescence	2	1	30 pgtv	1 min	15%	5%	TBD	None identified
Aqueous:								
Luminol Chemiluminescence	4	2 or 3	0.2 pgbm	Sampling limited	Envt.-Dependent	5%	4 pgbm	Oxidants/limited by blank variability
Catalase/Peroxidase Fluorimetry	4	3	0.2 pgbm	Sampling limited	10-15%	5%	5 pgbm	None identified/limited by blank variability
Chemiluminescence (peroxyoxalate)	2	3	TBD	NA	TBD	TBD	NA	NA
Acridan Fluorescence Quenching	2	3	~0.1 pgbm	Sampling limited	TBD	2%	NA	Apparently no interferences from oxidants, org. peroxides

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).

TABLE XVII.-ANALYTICAL CAPABILITIES FOR ANIONS

(Aqueous)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Interferences/ Constraints
SO_3^{2-}:				
Chemiluminescence	3	4	5 pgbm	None identified
Ion Chromatograph	4	4	300 pgbm	None identified
Automated Colorimetric Technique (Auto Analyzer)	4	4	1 ppm	
SO_4^{2-}:				
Ion Chromatograph	4	4	50 pgbm	None identified
Isotope Dilution	3	4	10^{-9} g	SO_3^{2-}, Sr^{2+}, Ba^{2+}
Automated Colorimetric Technique (Auto Analyzer)	4	4	1 ppm	
NO_3^-:				
Ion Chromatograph	4	4	100 pgbm	$SO_3^{=}$, Br^-: can be avoided
Direct UV Absorption	3	4	100 pgbm	Aromatics, Fe^{3+}; can be avoided
Automated Colorimetric Technique (Auto Analyzer)	4	4	1 ppm	
Cl^-:				
Ion Chromatograph	4	4	100 pgbm	None identified
Automated Colorimetric Technique (Auto Analyzer)	4	4	1 ppm	

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.

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TABLE XVIII.-ANALYTICAL CAPABILITIES FOR CATIONS

(Aqueous)

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Interferences/ Constraints
Ion chromatography for NH_4^+, Na^+, K^+	4	4	50 ppbm	minutes for analysis	None identified
Atomic Absorption for Ca^{++}, Mg^{++}	4	4	20 ppbm	minutes for analysis	None identified

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.

TABLE XIX.-ANALYTICAL CAPABILITIES FOR AEROSOL COMPOSITION

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Aerosol Sulfur:								
Filter Pack/IC[4] or other wet chemistry	4	3	0.3 $\mu g/m^3$	30 min	10%	6%	NA	Requires artifact-free filter medium
Flame Photometric Detector with SO_2 Denuder	4	1	1.5 $\mu g/m^3$	10 sec	20%	5%	10 $\mu g/m^3$	Loss of H_2SO_4/mass flow control required
FPD[5] with Heated Denuder for H_2SO_4	3-4	1	3 $\mu g/m^3$	1 min	20%	10%	10 $\mu g/m^3$	Mass flow required for airborne sampling
Heated Denuder for H_2SO_4	3	3	0.4 $\mu g/m^3$	8 hr	10%	5%	NA	None known
Low-pressure Impactor/Flash Volatilization-FPD	4	3	1 S/m^3 (6 ng S/stage)	1 hr	10-20%	5%	15 ng S	Coarse refractory S excluded, volatiles lost in low P stages
Aerosol Nitrate:								
Filter Pack/IC or other wet chemistry	4	3	0.2 $\mu g/m^3$	30 min	10%	5%	NA	Nitrate artifacts
Filter Pack with Predenuder for HNO_3	4	3	0.1 $\mu g/m^3$	30 min	15%	5%	20 $\mu g/m^3$	Coarse particle nitrate losses
Heated Denuder with CL Detector	3	2-3	0.1 $\mu g/m^3$	6 hr	15%	5%	NA	None known
Tungstic Acid Cartridge with C.L. Detector	3	3	0.1 $\mu g/m^3$	40 min	TBD	5%	5 $\mu g/m^3$	TBD

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).
[4]Ion Chromatography.
[5]Flame Photometric Detector (FPD).

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TABLE XIX.-Concluded

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Accuracy	Precision[3]	Calibration	Interferences/ Constraints
Soot Carbon Reflectance Photometry	4	3	20 ng/m^3	0.5-24 hr (variable)	15%	5%	NA	Possible interference from inorganic aerosols
Proton Inelastic Scattering	3	3	~20 ng/m^3	0.5-24 hr (variable)	10%	5%	NA	Requires uncommon facilities
Elemental/Metals Analysis:								
X-Ray Fluorescence (XRF)	4	3	0.1-10 ng/m^3	0.5-24 hr (variable)	10%	2%	NA	Various line overlap interferences can be eliminated
Proton-Induced X-Ray Emission (PIXE)	4	3	~0.5 ng/m^3	>0.5 hr	10%	5%	NA	Limited by elements in filter blank
Proton Inelastic Scattering (Light Elements)	3	3	10-50 ng/m^3	0.5-24 hr (variable)	10%	5%	NA	None known
Atomic Absorption Spectroscopy	4	3	~1 ng/m^3	>0.5 hr	10%	2%	NA	Matrix and interelement effects must be overcome
Inductively Coupled Plasma Emission	3	3	~1 ng/m^3	>0.5 hr	15%	10%	NA	Matrix and interelement effects must be overcome
Aerosol Strong Acid:								
Filter Extraction/pH	4	3	±0.1 pH	1 hr	15%	10%	NA	Coarse basic particles must be absent
Filter Extraction/Grand Titration	4	3	5 neq/m^3	1 hr	5%	2%	0.2 μ eq	Coarse basic particles must be absent
Filter/^{14}C Amine	3	3	<5 neq/m^3	3 hr	10%	5%	TBD	Coarse basic particles must be absent
Aerosol Ammonium:								
Tungstic Acid Cartridge with C.L. Detector	3	3	0.2 μg/m^3	40 min	TBD	5%	10 μg/m^3	TBD
Filter Extraction/Ion Selective Electrode	4	3	1 μg/m^3	30 min	10%	5%	10 μg/m^3	Loss or gain of NH_3 during sampling (NH_4NO_3)
Filter Extraction/Indophenol Colorimetry	4	3	0.2 μg/m^3	90 min	10%	5%	10 μg/m^3	Loss or gain of NH_3 during sampling (NH_4NO_3)
Aerosol Carbon:								
Thermoevolution/ Organic, Elemental	4	3	0.5 μg/m^3	6-24 hr	15%	10%	10 μg/m^3	Contamination problems with most filter media
Solvent Extraction (Organic)	4	3	1 μg/m^3	6-24 hr	20%	10%	NA	Lack of specificity for organics

[1](1) = Concept developed; (2) = Bench-top instrument; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.
[3]Standard deviation expressed as a percentage of clean-air tropospheric concentrations (under ideal conditions).
[4]Ion Chromatography.
[5]Flame Photometric Detector (FPD).

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TABLE XX.-ANALYTICAL CAPABILITIES FOR AEROSOL PHYSICAL PROPERTIES

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Interferences/ Constraints
Condensation Nuclei Technique (Pulsating)	4	1	D > 50 Angstroms Conc>10 cm^{-3}	2 sec	
Condensation Nuclei Technique (Continuous)	4	1	D > 500 Angstroms Conc>$10^{-2}cm^{-3}$	5 sec	
Electrical Mobility	4	1	D > 32 Angstroms Conc-size dependent	2 min	
Size Separation by Inertial Impaction/ Mass Determination by Quartz-Crystal Microbalance (QCM)	4	1	D ≥ 0.05 to 25 μm	30 sec	
Optical Scattering (White Light)	4	1	D > 0.3 μm-size particle		Index of refraction particle shape
Optical Scattering Laser Cavity	4	1	0.1 μm < D < 6 μm single particle		Index of refraction particle shape
Laser Scattering	4	1	0.3 < D < 32 μm		Index of refraction particle shape
Cloud and Precipitation Particles: Nephelometer (Integrated Optical)	4	1	D > 0.1 μm Conc>100 cm^{-3}	5 sec	
Transmissometers (Long Path)	4	1	D > 0.1 (path length dependent)	5 sec	
Laser Scattering	4	1	0.5 μm < D < 47 μm		Index of refraction particle shape
Laser Image (One-dimensional Shadow) - Type 1	4	1	10 μm < D < 300 μm		Index of refraction particle shape
Laser Image (One-dimensional Shadow) - Type 2	4	1	150 μm < D < 12 mm		Index of refraction particle shape

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.

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TABLE XXI.-ANALYTICAL CAPABILITIES FOR CLOUD CONDENSATION NUCLEI

Technique	Development[1] Status	Sampling[2] Mode	Detection Limit	Time Resolution	Interferences/ Constraints
Static Diffusion Chamber-Integrated Light Scatter Detector	3	1	20 cm^{-3} 0.25 < S(%) < 2%	45 sec	Large insoluble particles
Continuous-Flow Diffusion Chamber Single-Particle Optical Detector	3	1	0.02 cm^{-3} 0.1 < S(%) < 2	5 min	Large insoluble particles
Isothermal Haze Chamber Single-Particle Optical Detector	3	1	0.02 cm^{-3} 0.01 < S(%) < 0.25	5 min	Large insoluble particles

[1](1) = Concept developed; (2) = Bench-top instruments; (3) = Laboratory prototype available for field testing; and (4) = Field-tested or commercial instrument.
[2](1) = Continuous, real time; (2) = Continuous, integrative; (3) = Intermittent; and (4) = Remote.

TABLE XXII.-MARINE BOUNDARY LAYER EXPERIMENT

Experiment Module #	Experiment Quantity	Priority	Minimum Detection Limit	Minimum Sampling Time
1	$(CH_3)_2S$, H_2S, CS_2	A	5-10 pptv	20 min
	SO_2	A	5-10 pptv	"
	OCS	B	50-100 pptv	"
	NH_3	B	10 pptv	"
	H_2O_2	B	100 pptv	"
2	SO_4^{2-} (total) aerosol	A	0.3 $\mu g/m^3$	20 min
	SO_4^{2-} (<0.1 μm) aerosol	B	0.2 $\mu g/m^3$	40 min
	size distribution (0.01-10 μm)	A	---	20 min
	total [nuclei] (≥0.01 μm)	B	10/cm^3	1 min
	NH_4^+ (aerosol)	B	0.2 $\mu g/m^3$	20 min
	ccn (1.01 ≤ S ≤ 1.2)	B	0.02/cm^3	20 min
	elemental carbon	B	0.01 $\mu g/m^3$	40 min
	^{222}Rn, ^{210}Pb, ^{210}Bi	A	---	20 min
	$^{34}S/^{32}S$	B	---	40 min
	Na^+, Cl^-	A	0.5 $\mu g/m^3$	20 min
3	SO_4^{2-} cloud (total)	A	0.5 μM	20 min
	H_2O_2 (aq)	B	0.1 μM	"
	NH_4	B	1 μM	"
	pH	B	---	"
	cloud water	B	0.1 g/m^3	"
	cloud drop size	B	1 μm	"

Module 0 = Global Tropospheric Experiment

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TABLE XXII.-Concluded

Experiment Module #	Experiment Quantity	Priority	Minimum Detection Limit	Minimum Sampling Time
4	HNO_3	A	10 pptv	40 min
	NO_3, PAN	B	10 pptv	"
	HO_2NO_2, N_2O_5	B	10 pptv	"
	NH_3	B	10 pptv	"
5	NO_3^- (aerosol total)	A	0.2 $\mu g/m^3$	40 min
	NH_4^+ (aerosol total)	A	0.2 $\mu g/m^3$	"
6	NO_3^- cloud (total)	A	1 μM	40 min
	NH_4^+	A	1 μM	"
	NO_2^-	B	1 μM	"
	pH	A	---	"
	Cl^-	A	1 μM	"
	cloud water	A	0.1 g/m^3	"
	cloud drop size	A	1 μm	"
7	HCHO, RCHO	A	10 pptv	20 min
	HCOOH, RCOOH	A	100 pptv	"
	HPBC	B	100 pptv	"
	PAN	B	10 pptv	"
	VOM	B	---	"
	HO_2	B	10 pptv	"
8	Organic C aerosol (total)	A	0.1 $\mu g/m^3$	20 min
	Organic film	b	---	"
	Elemental C	B	0.01 $\mu g/m^3$	"
9	$HCOO^-$	A	1 μM	20 min
	$RCOO^-$	A	1 μM	"
	Polyorganics	B	---	"
	HCHO, HCHO-S(IV)	A	1 μM	"
	RCHO, RCHO-S(IV)	A	1 μM	"
	S(IV)	A	1 μM	"

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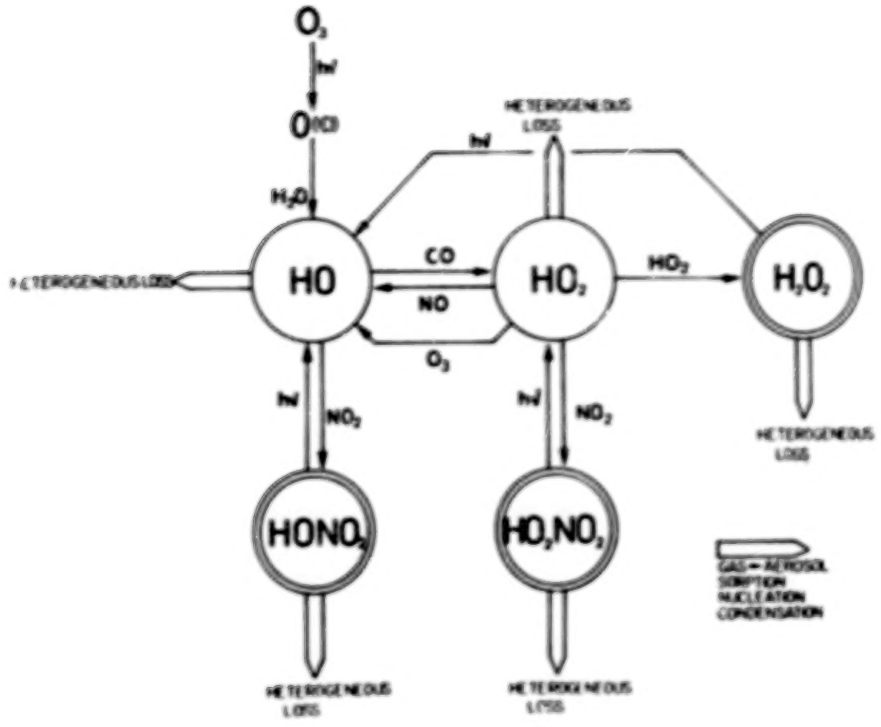

Figure 1.- Heterogeneous tropospheric chemistry: major atmospheric reactions of H_xO_y species. The circle indicates products undergoing predominantly cyclic transformations, the double circle indicates products undergoing predominantly noncyclic transformations, the arrow indicates gas-phase reactions, and the double arrow indicates loss reaction from the gas phase.

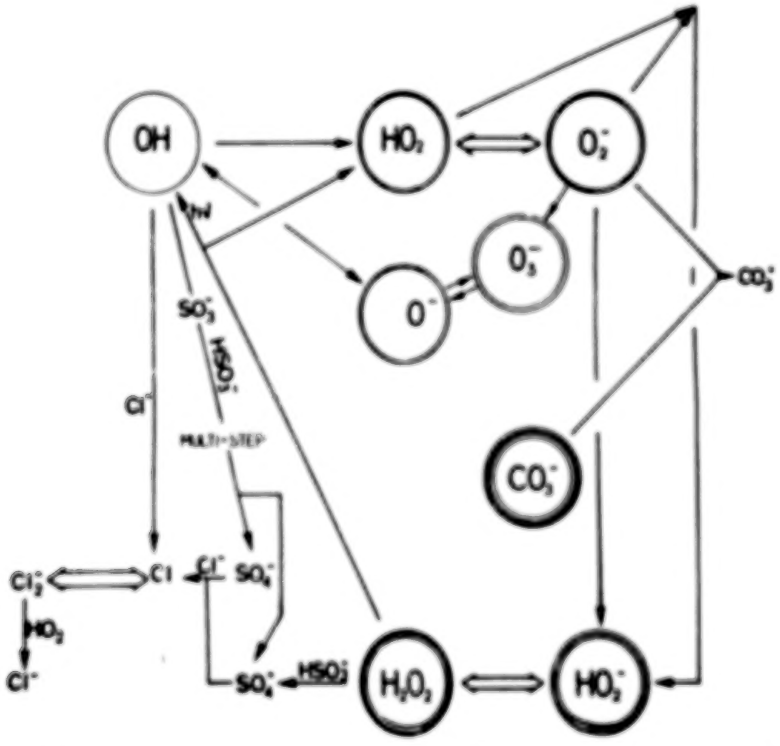

Figure 2.- Heterogeneous tropospheric chemistry: proposed chemical pathways inside cloud droplets.

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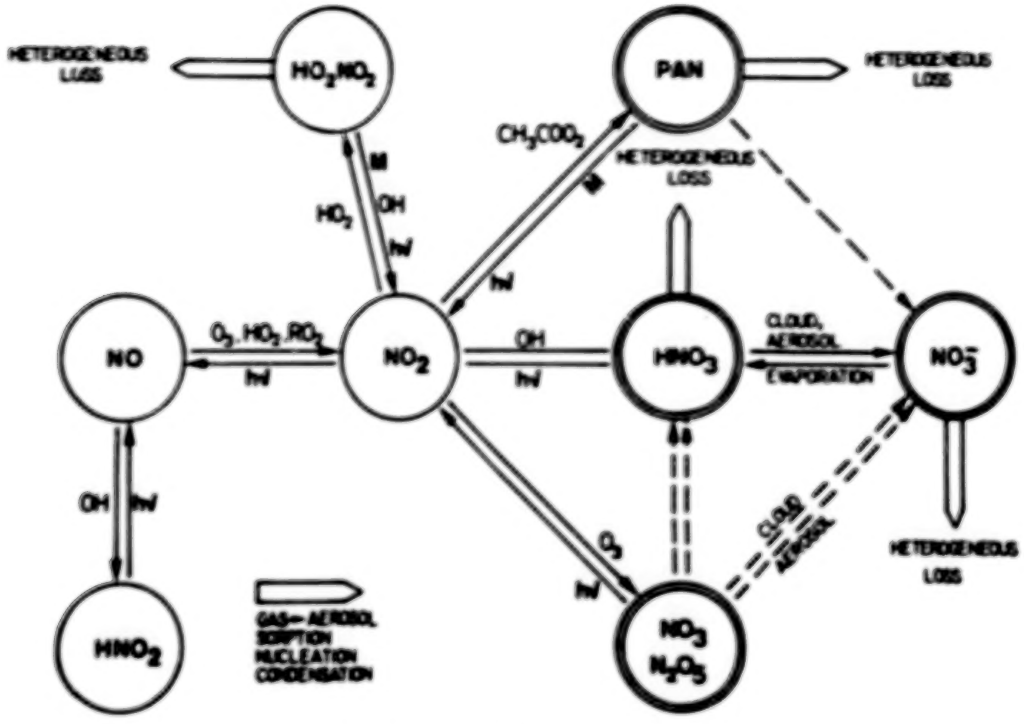

Figure 3.- Heterogeneous tropospheric chemistry: major atmospheric reactions of N_xO_y species. The circle indicates products undergoing predominantly cyclic transformations, the double circle indicates products undergoing predominantly noncyclic transformations, the arrow indicates gas-phase reactions, and the double arrow indicates loss reaction from the gas phase.

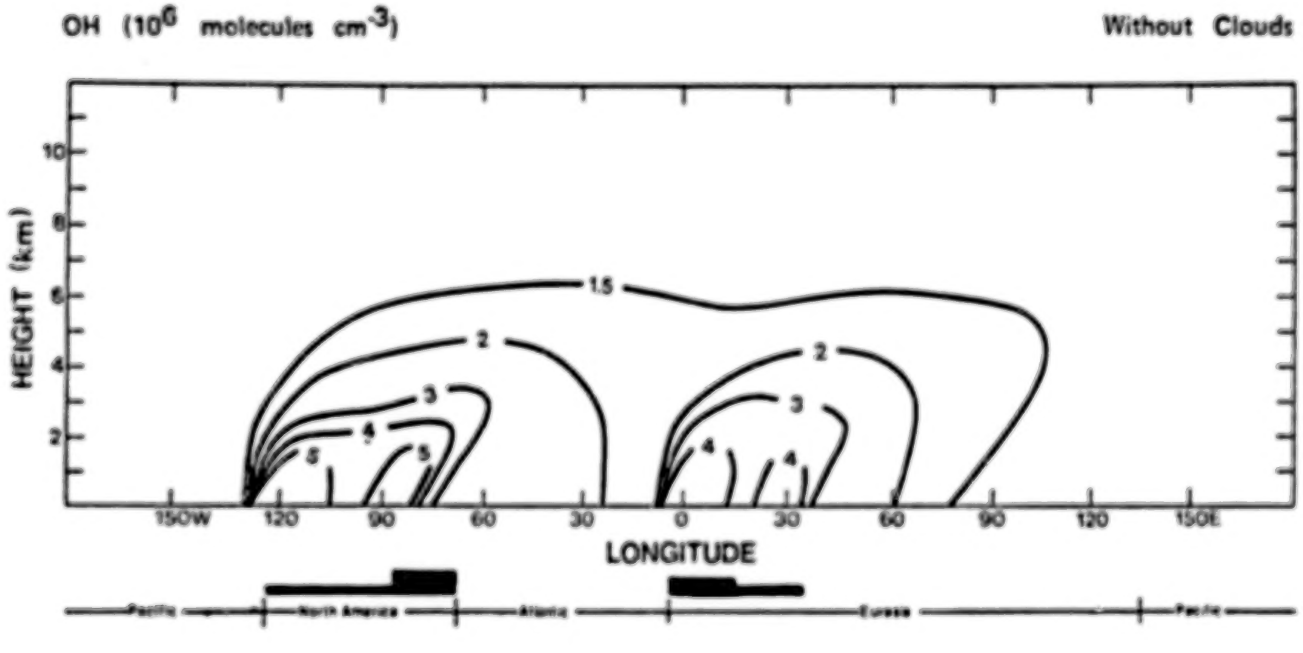

Figure 4.- Model calculation of daytime average OH concentration along the 45°N latitude in July, diffusive vertical transport only. The emission profile for CO over North America and Europe is indicated by the black bar graph. The NO_x emissions are assumed to be 5 percent of CO emissions. (Gidel, 1983.)

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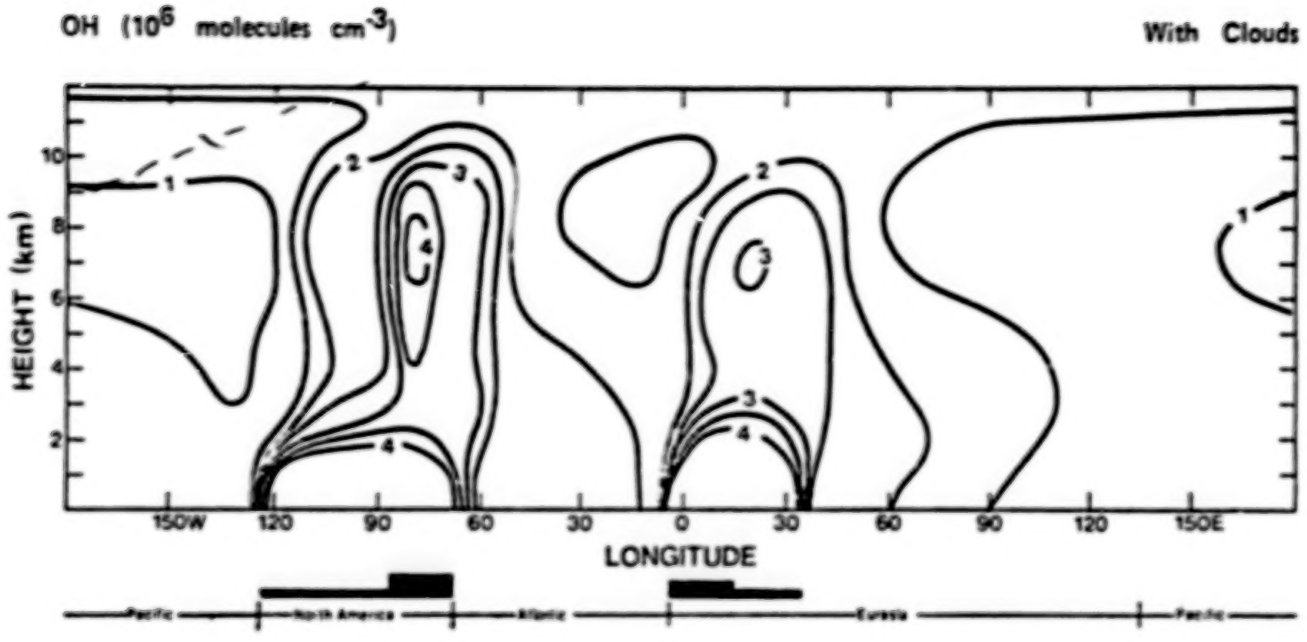

Figure 5.- Model calculation as shown in figure 4 except with vertical transport enhanced by cloud venting. (Gidel, 1983.)

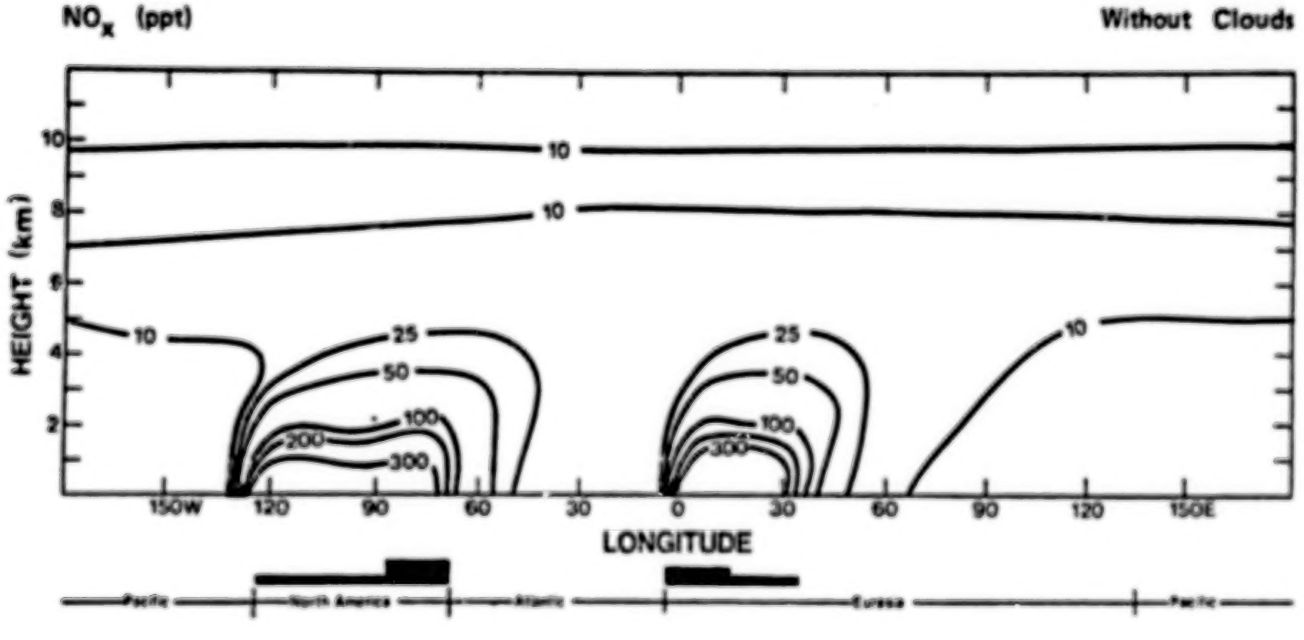

Figure 6.- Model calculation of daytime average NO_x concentration. July conditions are at 45°N with diffusive vertical transport only. The emission profile for CO over North America and Europe is indicated by the black bar graph. The NO_x emissions are assumed to be 5 percent of CO emissions. (Gidel, 1983.)

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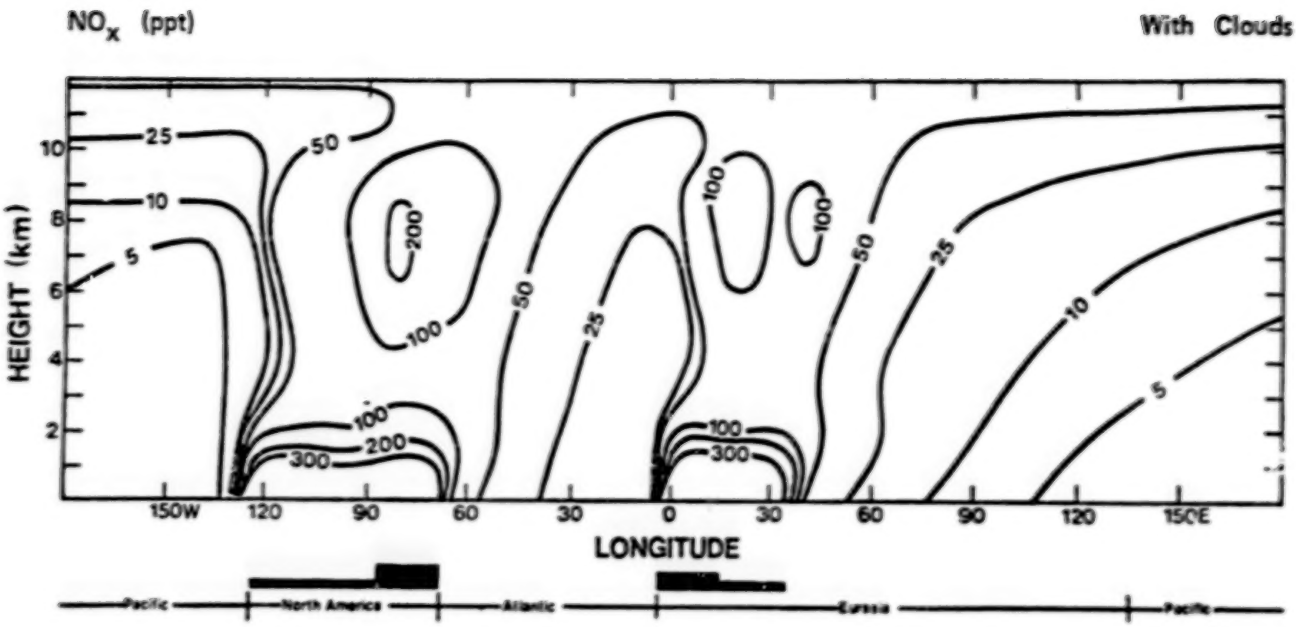

Figure 7.- Model calculation as shown in figure 6 except with vertical transport enhanced by cloud venting. (Gidel, 1983.)

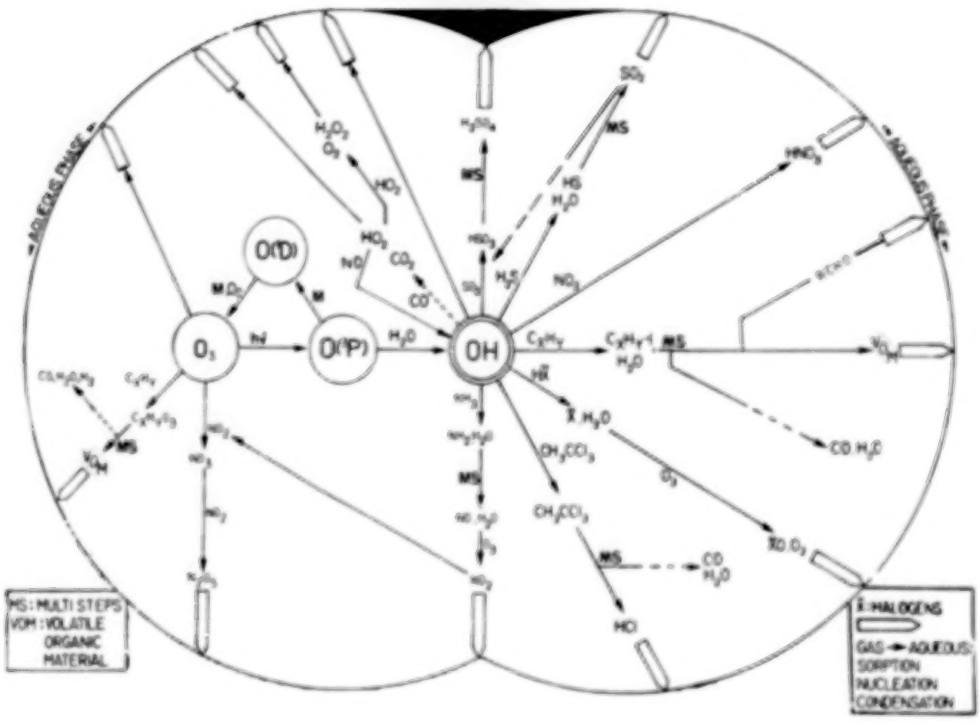

Figure 8.- Heterogeneous tropospheric chemistry: phase transitions.

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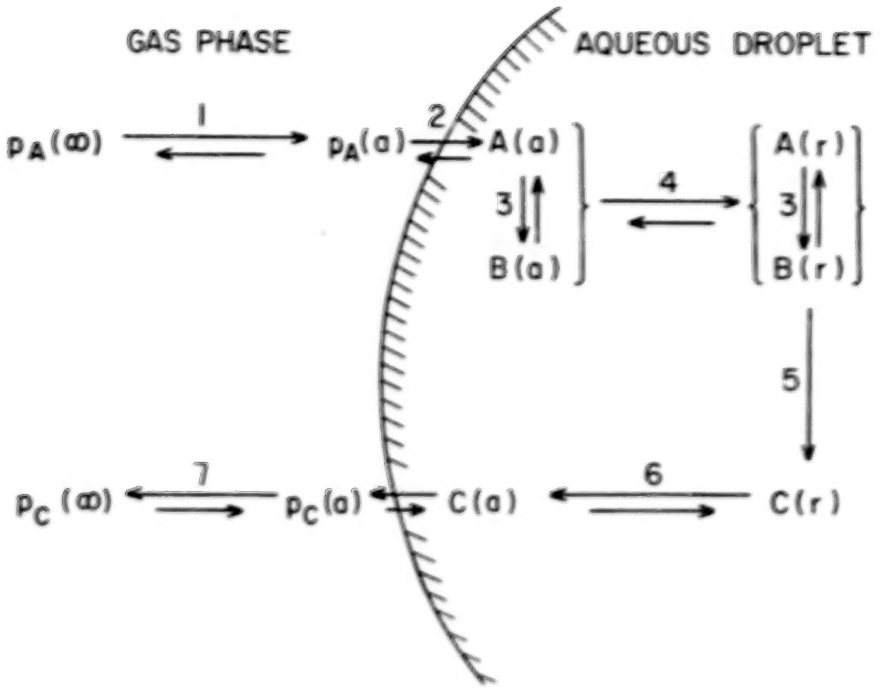

Figure 9.- Schematic illustration of the subprocesses comprising the overall gas-aqueous reaction process under examination in this paper. Numbers labeling the several processes correspond to the listing presented in the text. The parameter A represents concentrations of aqueous-phase reagent species transferred from the gas phase; B represents the species in rapid equilibrium with A; and C represents the product species at the surface of the drop (a) or in the interior (r). The parameters P_A and P_C represent gas-phase partial pressures of A and C at the surface of the drop (a) and at large distances from the drop (∞). (Schwartz, 1983.)

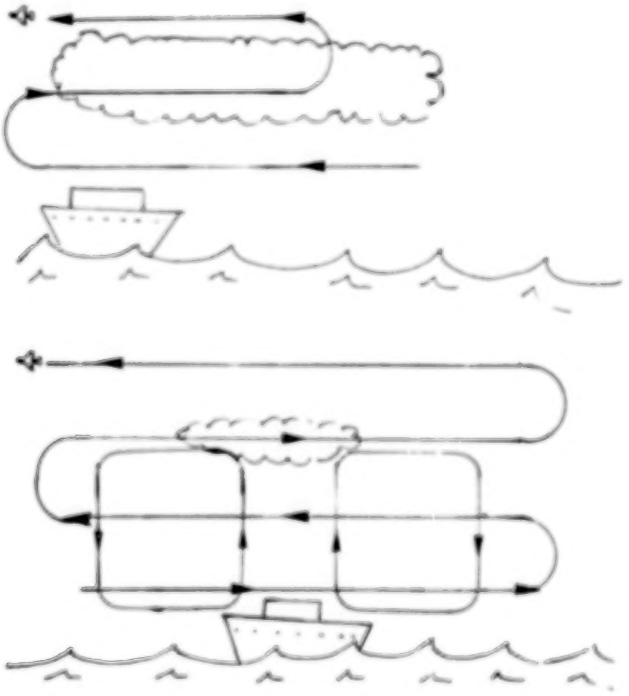

Figure 10.- Marine boundary layer experiment.

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16. Abstract

The role of heterogeneous reactions and processes in the troposphere has been critically assessed by a group of 30 experts from government, universities, and industry. The results of this assessment, including identification and prioritization of a number of important and scientifically tractable reactions and processes, as well as recommendations of ways in which they can be incorporated into the existing NASA tropospheric chemistry program are presented. Also presented is a detailed summary of the considerations that led to the group's recommendations.

The key cycles in tropospheric chemistry, including those for nitrogen, sulfur, carbon, and the halogens, are described to the extent possible with the present level of understanding, and data needed to remove conceptual uncertainties and/or to improve quantitative predictive capabilities are noted.

Research programs suggested include: (1) field studies of important atmospheric problems that have potentially significant heterogeneous components such as cloud chemistry and transport, the marine boundary layer, and emissions from biomass burning, (2) laboratory experiments to obtain needed thermal and kinetic data, and information about mechanisms for nucleation and growth processes, (3) modeling efforts to incorporate field data for predictive purposes in cloud droplet chemistry, cloud microphysics, and phase transitions, and (4) technological development of a number of new instruments required for obtaining precise field data. Establishment of an instrument review panel is also recommended.

Modes for integrating new types of research into existing NASA programs over a 10-year period are proposed. This includes phasing technology-limited portions of the research into existing programs in conjunction with the development of appropriate technology and field measurement techniques.

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